THE STUDY OF CRYSTAL GROWTH WITH THE ELECTRON MICROSCOPE

Thesis submitted to the University of Glasgow
for the degree of Ph.D.
by
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I - PREFACE

PREFACE.

The idea that crystals were made up of regular building units was put forward as early as 1784 by Haüy. Despite this early recognition of a regularity in the construction of crystals, almost a full century elapsed before any speculation arose on the nature of the crystal growth process. From Haüy's idea developed the conception of a crystal as a three dimensional array of particles, but even this concept did not lead to any consideration of crystal growth as a process involving the addition of these particles.

Indeed the earliest theories of crystal growth put forward by Gibbs (1878) and Curie (1885) were arrived at from purely thermodynamic considerations. The atomic theory of crystal growth, in which the process is regarded as the addition of atoms or molecules to the growing crystal face, developed much later with the work of Volmer (1921), Kossel (1927) and Stranski (1928), who did however make considerable use of some of the ideas embodied in earlier theories. Despite this new viewpoint, the protagonists of the atomic theory of growth made experiments of the same type as the workers on the purely thermodynamic theories. These experiments consisted chiefly of growth rate measurements. Some studies of the growth surface

were made but these suffered from the many limitations of the experimental methods then available. Accordingly there accrued none of the information on fine surface structure which would have led to a greater understanding of the crystal growth process.

The classical experiment on crystal growth was performed by Volmer and Schultze (1931), who measured the growth rate of iodine crystals from the vapour. Their theory postulated that a crystal grew layer by layer, a fresh layer being formed as soon as one was completed. Volmer and Schultze believed that their results lent support to this surface nucleation theory. However Burton, Cabrera and Frank (1949) re-examined the classical theory and showed that in fact the data of Volmer and Schultze provided a powerful argument against it. They demonstrated that the theory involved the existence of a critical supersaturation for continued crystal growth, whereas the experimental data showed that continued growth occurred at supersaturations far below this critical value.

Frank (1949) pointed out that all the earlier theories had assumed the existence of perfect crystals. However analysis of crystal structures by X-ray diffraction (as originally suggested by von Laue (1912)) and tensile strength measurements on metal crystals had

both yielded evidence which showed that crystals were far from perfect. Taylor (1934) and Orowan (1934) and Burgers (1939) had classified these imperfections in terms of dislocations of two types : edge dislocations and screw dislocations. Frank suggested a spiral growth theory based on the existence of screw dislocations in a growing crystal. In essence this theory involves the existence of a continuous growth layer on the surface of a growing crystal. There is thus no necessity for the continuous formation of fresh layers and as a result the critical supersaturation for growth to continue is much lower on the basis of this theory. In fact the critical value predicted from this theory is in agreement with the experimental value.

By this time two powerful methods of examining surface structure had become available. These were phase contrast and electron microscopy. Theoretically the latter is probably the more powerful, since it yields information on the molecular scale in three dimensions, whereas phase contrast microscopy only gives molecular resolution in one dimension. However the difficulty of preparation of specimens for the electron microscope means that valuable information can be obtained from phase contrast microscopy in cases where electron microscopy is inapplicable. As a result the

the two methods may be regarded as complementary. The work described in this thesis is based on electron microscopy but it should be remembered that information obtained from phase contrast microscopy has been applied to these results to yield many useful ideas.

Frank's theory received striking confirmation from observations based on both these methods. Using phase contrast, Griffin (1949) reported spiral markings on beryl crystals, while with the electron microscope Dawson and Vand (1951) showed the existence of spirals on crystals of a paraffin hydrocarbon. These patterns bore a startling resemblance to those predicted theoretically by Frank.

It was noted earlier that two approaches were taken in the classical work on crystal growth, namely the atomic and the thermodynamic, and it was seen that appreciable progress was only made on the synthesis of these two methods of appraach. A similar position may be said to exist today. Crystal growth can be described and investigated in terms of the geometrical and thermodynamic properties of screw dislocations and growth spirals. It can also be described from a chemical or molecular viewpoint by considering the addition of molecules to spiral growth steps. As before valuable results can be obtained from both methods.

Recent workers in this field (e.g. Forty 1952a)

have found that it is possible to obtain spiral features of a size sufficiently large to enable them to be observed in the optical microscope. Thus several optical studies have been carried out on crystal growth and since these cannot give information on the molecular scale, this work has tended to lead to the development of the "geometrical approach". This also applies to some phase contrast studies since these methods may also yield information which is not entirely on the molecular scale. The spiral growth theory could plainly not have advanced without this development of the geometrical appreach and indeed much of the earlier work with the electron microscope has also assisted in the development of this approach (e.g. Dawson and Vand 1951, Dawson 1952 and Anderson and Dawson 1953).

However having developed the theory from this standpoint it is important not to lose sight of the chemical or molecular viewpoint. This is particularly significant in view of the fact that, whereas the Frank theory in its original form was concerned with growth from the vapour, most of the recent experimental work has involved growth from solution. Although the differences involved are slight there are one or two additional factors such as association to be considered: it is thus necessary to adopt the molecular viewpoint and discuss the aggregation of the molecules in solution.

II - INTRODUCTION

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(1) HISTORICAL DEVELOPMENT OF THE CLASSICAL THEORIES.

All theories of crystal growth prior to the Frank dislocation theory are described as classical. The classical theories will be considered under three headings : (i) Thermodynamic theories, (ii) Diffusion theories and (iii) Kinetic and atomic theories. This is not to be taken as a rigid classification since the major achievements of the classical theory are based on a synthesis of ideas from all three categories.

Thermodynamic theories.

The first theories of crystal growth were put forward at the end of the last century and were based on purely thermodynamic considerations. As in all thermodynamic treatments no extra account is taken of atomic and molecular considerations. Accordingly the atomic arrangement in crystal surfaces is neglected.

Curie (1885) may be said to have originated the first more or less complete theory of crystal growth, although Gibbs (1878) had previously studied the relationship between crystal form and surface energy. Gibbs, while appreciating the difference between the two cases, considered a growing crystal as analogous to a liquid drop and applied the results of his thermodynamic studies to this problem. The surface energy of a liquid drop

tends to attain a minimum value and accordingly Gibbs postulated that for a crystal nucleus in equilibrium with its vapour, $\sum_{i=1}^{n} \sigma_i F_i$ = constant, where σ_i = the surface energy and F_i is the area of the i^{th} face of a n-faced crystal.

Curie (1885) actually based his ideas on the Gauss capillarity theory which deals with the work performed in capillary phenomena. If the energy required to increase the i^{th} surface above by unit area is E_i, then Curie states that the final crystal form is such that $\sum_{i=1}^{n} F_i E_i$ attains a minimum value. On the basis of this theory the predominant faces of a crystal are those for which E_i is smallest (or as Curie puts it, those for which the capillarity constant is smallest). The Gauss theory is only strictly applicable to liquids which can be subjected to deformation processes quite impossible for crystals. Curie's circumvention of this difficulty involves certain assumptions of doubtful validity and the chief weakness of the theory lies in this direction. He describes an equivalent deformation process in which material is shifted from one face to another on the surface of a crystal in saturated solution. Curie proceeds to determine theoretically the surface forms of various types of crystal.

Some of the first experimental measurements on growth rates are due to Wulff (1901). From these

experiments he obtained the result known as Wulff's theorem which states, in essence, that the rate of outward extension of a face is proportional to the length of the normal drawn to the face from ~~the centre of~~ a point within the crystal. He related the length of the normal to the surface free energy of the face and thus showed that the growth velocity of the face was proportional to its surface free energy. Since the predominant faces will be those with the smallest growth velocity and therefore the smallest free energy, it is seen that Wulff's theorem is just an alternative statement of the Curie concept.

Marc and Ritzel (1911) modified the Curie theory and stated that under the influence of "solution pressure" the crystal is forced to favour the more soluble faces, the less soluble vanishing. The "solution pressure", which is measured by the solubility of isolated faces, has different values in different directions. This modification means, in effect, that an augmentation of one face is only gained at the expense of another. The theory has the advantage that it is no longer necessary to transfer material in bulk over the surface of a crystal in barely saturated solution. On the other hand there is no more evidence for solution pressure differences of this kind than there is for a bulk transfer of the type envisaged by Curie.

The Curie theory eventually collapsed after the criticisms of Berthoud and Valeton. Berthoud (1912) pointed out that the theory implied that growth should be more rapid at higher supersaturations and as a result the crystal habit should become more complex, whereas it is known that the reverse is the case. Valeton (1924) adapted the work of Gibbs to the Curie theory. Gibbs (1878) had pointed out that his surface energy relation only applied to a crystal in equilibrium and he considered that it was only of value in studying the growth of minute crystals. Valeton confirmed this by demonstrating that for larger crystals the surface energy had a negligible effect on growth. The thermodynamic theories are thus unable to deal with growth in conditions removed from equilibrium. To study this problem it is necessary to introduce ideas from outwith the field of thermodynamics.

Diffusion theories.

Simultaneously with the thermodynamic theories there developed the diffusion theories which considered crystal growth as a diffusion phenomenon.

Among the earlier theories of this group was that of Noyes and Whitney (1897) which was mainly concerned with the dissolution of crystals and not the complementary process of growth. A later theory was that of Nernst (1904). Both these theories involve the existence of a

diffusion layer adjacent to the crystal. The process at the surface is imagined to be one of infinite rapidity and the surface concentration is supposed to have the saturation value, there being a diffusion gradient to the outer edge of the layer where the concentration has the same value as that prevailing in the bulk of the solution.

However Miers (1903) measured the refractive indices of solutions at crystal surfaces by an internal reflection method and showed that the supersaturation was greater near the crystal than in the bulk of the solution. The diffusion theories were thus largely discredited.

Kinetic and Atomic theories.

All the later theories of the classical period utilise kinetic methods and in common with all kinetic treatments take account of atoms and molecules. The general practice is to use the terms "kinetic" and "atomic" as alternatives in the designation of this group. It might, however, be better to describe the theories of Volmer (1921), Brandes (1927) and Becker and Döring (1935) as "kinetic" and reserve the term "atomic" for those of Kossel (1927) and Stranski (1928, 1931), which emphasise the atomistic nature of crystal growth.

The essential difference in approach of the thermodynamic and kinetic theories may usefully be

summarised here. The thermodynamic theories consider the equilibrium $nA \rightleftharpoons A_n$, between n single groups A and one multiple group A_n. The kinetic theories on the other hand consider the rates of increase and decrease in size of a crystal which is considered as a liquid drop. The advantage of the kinetic theories is that unlike the thermodynamic theories, they allow the study of systems which are removed from equilibrium.

The first kinetic theory was the adsorption layer theory of Volmer (1921) which was prompted by his studies on the layer growth of mercury. The main principle of the theory is that a particle arriving at a crystal surface only loses a portion of its latent heat. Thus although it is effectively bound to the crystal surface, it still possesses considerable freedom of lateral movement. An adsorption layer is thus created from many such particles. Volmer is able to explain the formation of thin tabular crystals on this basis.

Brandes (1927) related the growth rate of a surface to the work of formation of a two dimensional seedling which is large enough to survive on the surface without evaporation. He considers that this, rather than the surface free energy is the predominant factor controlling growth. He assumes that the outward growth of a seedling to form a complete layer is rapid compared to the formation of the seedling, which is thus

the rate determining stage in continued growth of an existing crystal. He utilises the liquid drop analogy and by calculating the work done in transferring material from an infinitely large mass to a small disc, he is able to determine the work of formation of a seed at various supersaturations.

Backer and Döring (1935) considered the interrelation of these two dimensional seeds or nuclei and the old established three dimensional seeds necessary for initial formation of a crystal. They calculated the supersaturations required for (i) nucleation of a three dimensional crystal seed from the vapour, (ii) nucleation of a liquid drop from the vapour and (iii) nucleation of a two dimensional seed. They found that these supersaturations were in the ratio 10 : 5 : 1.5. Thus before a crystal can be formed at all, a high supersaturation is required to produce a nucleus. The continued growth of this crystal requires a supersaturation high enough to allow the creation of two dimensional nuclei every time a layer in the crystal is completed. Provided there is a ready supply of these the crystal will grow out rapidly layer by layer.

Before considering the theories of Kossel (1927) and Stranski (1928, 1931), which involve the fine structures of surfaces, it is necessary to review earlier theories of this nature.

Bravais (1866) had postulated that the growth velocity of a plane was proportional to the density of the lattice points (reticular density) in the plane. The predominant faces in growth are those of greatest density i.e. the close packed faces.

Soehncke (1879) accomplished the synthesis of the Bravais and Curie theories by postulating that the faces with the greatest reticular density have minimum surface energy.

Niggli (1920) extended the Bravais theory by relating the reticular density to the wideness of separation ("spacing") of the lattice planes. By considerations of this nature he was able to account for certain residual phenomena unexplained by the Bravais theory.

The theories of Kossel (1927) and Stranski (1928, 1931) are generally treated as one, but it should be noted that whereas Stranski believes his theory can be reconciled with those of Volmer and Brandes, Kossel denies the possibility of any such synthesis.

Kossel postulates that a crystal grows by the repeated addition of equivalent units to the growing crystal. He states that the energy release in the addition of these equivalent steps (wiederholbare Schritte) is the same in all directions. He divides the attachment energy ϕ_o of an equivalent step into three portions - two of these, ϕ' and ϕ'' are tangential

to the normal growth direction (i.e. parallel to the surface of the crystal) and the third, ϕ''' is parallel to it. However when a lone particle settles on the surface to begin a new row adjacent to a complete row (e.g. at site A in Fig. 1, page 15) the energy release is only $\phi'' + \phi'''$. Further the energy release associated with the initiation of a new layer on the crystal (e.g. at B) is only ϕ'''.

Kossel proceeds to work out the energies associated with the deposition of units on the most important positions of a cube in terms of ϕ', ϕ'' and ϕ'''. These have to be calculated separately for homopolar and heteropolar crystals.

Stranski (1928, 1931) considers that the energy of separation of a particle from its position on the crystal surface is the essential criterion for assessment of the probable character of the growth process. The particles which require the greatest work for separation will obviously retain their positions for the longest time. Conversely new particles will tend to condense on such sites. He calculates the energy of attachment as the algebraic sum of an electrostatic attraction term and a repulsion term. He is then able to calculate the energies of attachment for 27 positions on a cube. Like Volmer, Stranski considers growth from the vapour in contrast to Kossel who deals with growth from solution.

Stranski later modified his theory to take

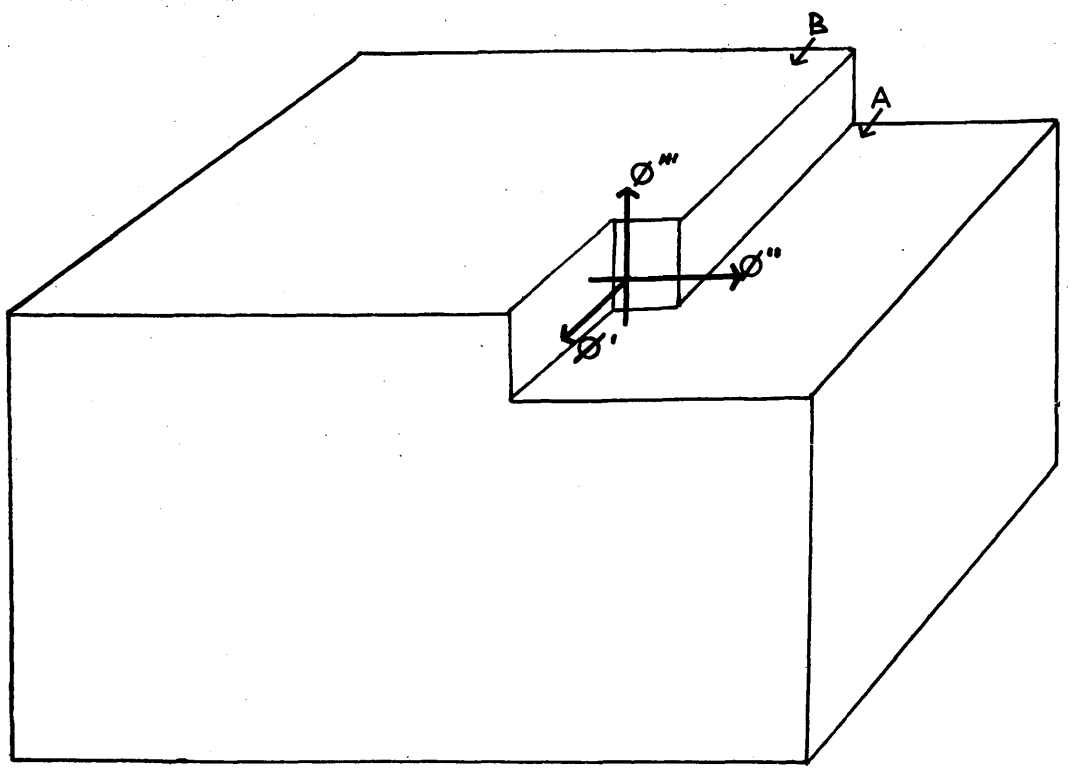

Fig. 1

Kossel's theory : the diagram shows the attachment energies in the axial directions. Condensation on sites such as A involves only ø'' and ø''', while condensation at sites such as B involves only ø'''.

account of the two dimensional seeds proposed by Brandes (1927). Stranski and Kaischew (1935, 1937) calculate the connection between the sizes of the two and three dimensional nuclei, working from lattice energy considerations. They obtained the result that a two dimensional seed need only be half the size of a three dimensional one, to survive at the same supersaturation.

Considering the classical theories as a whole then, the principal idea is seen to be that continued growth involves renucleation by formation of a two dimensional seed every time a layer is completed on the crystal surface.

(2) MATHEMATICAL FORMULATION OF THE CLASSICAL THEORY.

In their re-examination of the classical theory Burton and Cabrera (1949) (also Burton, Cabrera and Frank 1951) have given a mathematical treatment which embodies the ideas expressed by Volmer (1921), Stranski (1931) and Becker and Döring (1935). The derivation given here is a modified version of their treatment.

Work done in formation of critical nucleus.

Suppose we consider the addition of dn molecules to a square two dimensional nucleus containing n molecules.

Decrease in free energy (-dG) = work done by system

i.e. $-dG$ = -(work done on nucleus against edge free energy in increasing surface)

+(work done by vapour in transferring to nucleus) (1)

Now if edge free energy / unit length be represented by σ and a nucleus of edge length l is transformed to one of edge $l + dl$ by addition of dn molecules, then:

Work done in expansion against edge free energy

$= \sigma \times$ increase in perimeter

$= \sigma \times 4dl$

The second term in equation (1) may be considered as the free energy released on condensation of dn molecules i.e. $dn.e'$, where e' is the free energy released by one molecule on condensation.

$$\therefore -dG = -\sigma \times 4dl + dn.e' \qquad (2)$$

Now if a^2 is the area occupied by one molecule, since l^2 is the surface area of the nucleus containing n molecules,

$$n = \frac{l^2}{a^2}$$

$$\therefore dn = \frac{2l}{a^2} dl$$

Thus we may rewrite equation (2) :

$$+dG = 4\sigma dl - \frac{2l}{a^2} dl\, e'$$

Now the critical nucleus is in unstable equilibrium with the system and any slight disturbance in the equilibrium can occur spontaneously and will lead to a decrease in free energy. Thus the free energy has a

maximum value when $l = l_c$, where l_c is the edge length of the critical nucleus.

$$\text{i.e. } dG = 0 \text{ when } l = l_c$$

$$\therefore 4\sigma dl = \frac{2l_c}{a^2} dl\, e'$$

$$\therefore \quad \underline{l_c = \frac{2\sigma a^2}{e'}} \qquad (3)$$

From (2) $dG = 4\sigma dl - dn\, e'$ and we may obtain G_c the free energy of the critical nucleus by integrating between the limits 0 and l_c, 0 and n_c, where n_c is the number of molecules in the critical nucleus:

$$G_c = \int_0^{l_c} 4\sigma dl - \int_0^{n_c} e'\, dn$$

$$= 4\sigma l_c - n_c e'$$

$$= 4\sigma l_c - l_c^2 \frac{e'}{a^2}$$

(since $n_c = l_c^2 / a^2$)

$$= \frac{8\sigma^2 a^2}{e'} - \frac{4\sigma^2 a^2}{e'}$$

(using the value of l_c in (3))

$$\therefore \quad \underline{G_c = \frac{4\sigma^2 a^2}{e'}} \qquad (4)$$

Since the total edge free energy of the critical nucleus is $\sigma \times 4l_c = \frac{8\sigma^2 a^2}{e'}$ it is seen that the free energy of formation of the critical nucleus is equal to half the edge free energy. This result was obtained by Brandes using a slightly different approach.

To determine G_c it is therefore necessary to know the value of e', the energy released in the condensation of one molecule or, alternatively, the work done

in transporting a molecule from the vapour to the nucleus. We may consider this to be executed by expanding the gas so that its pressure changes from p, the pressure of the surrounding vapour, to p_o, the vapour pressure when solid and gas are in equilibrium.

The work done in this process is given by the expression $kT \ln \frac{p}{p_o} = kT \ln \alpha$, where k is Boltzmann's constant and α is the supersaturation ratio.

Now since no free energy is expended in transforming vapour at the equilibrium pressure to the solid state, we may write :

$$e' = kT \ln \alpha \quad , \text{ neglecting any}$$

effects due to diffusion effects or an adsorption layer.

Substituting this value in (4):

$$G_c = \frac{4\sigma^2 a^2}{kT \ln \alpha} \qquad (5)$$

Now it is assumed that the edge free energy results from the "unsaturated" bonds at the surface of the crystal. Each molecule possesses one of these. Thus if the nearest neighbour interaction is ϕ, then the energy of such an unsaturated bond, and therefore the edge free energy per molecule, is $\frac{1}{2}\phi$. Since one molecule occupies an area a^2, a molecule at the surface may be considered to have a surface "frontage" of a.

$$\therefore \frac{1}{2}\phi = a\sigma$$

$$\therefore \quad 4a^2\sigma^2 = \phi^2$$

and thus from (5): $$G_c = \frac{\phi^2}{kT \ln \alpha} \qquad (6)$$

This equation is similar to that obtained by Becker and Döring (1935) using a slightly different method.

Rate of nucleus formation.

Nuclei are obviously formed by molecules striking the surface of the growing crystal. However only a fraction of the molecules striking the surface will form nuclei, because of the relatively high energy of formation, G_c, of the nuclei. We may regard this energy as a type of activation energy and thus:

Rate of formation of nuclei = (No. of molecules striking surface) x (fraction with sufficient energy)

$$= Z\,s \quad x \quad e^{-G_c/kT},$$

where Z is the number of molecules striking an area of one square centimetre in one second and s is the surface area of the crystal.

Using the value of G_c from (6) we obtain the expression :

$$R = Z\,s\,e^{-\left(\frac{\phi}{kT}\right)^2 / \ln\alpha} \qquad (7)$$

Rate of growth.

Since at least one nucleus is required to initiate the growth of one layer and since the rate of completion of layers is assumed to be very great compared to the rate of initiation, the maximum rate

of growth (expressed in layers per second) can be taken equal to the rate of nucleus formation:

$$V_{max} = Z s e^{-\left(\frac{\phi}{kT}\right)^2 / \ln \alpha} \qquad (8)$$

(3) THE CLASSICAL EXPERIMENT OF VOLMER AND SCHULTZE.

The experiment of Volmer and Schultze (1931) is described as the classical experiment, since it is typical of all the classical experiments and also because it was regarded as a convincing experimental verification of the Volmer adsorption layer theory.

The apparatus consisted of two bulbs at the end of a U-tube which was immersed in Dewar flasks containing ice at $0^{\circ}C$. The bulbs both contain iodine crystals. The system is pumped out so that the crystals are in contact with their own vapour only. The temperature of the bulb on the ~~left~~ right hand side is then ~~raised~~ decreased slightly ~~by an electrical heater~~ so that iodine sublimes from the left hand bulb and condenses on the crystals in the right hand bulb. The growth rate of these crystals is measured microscopically. Observations are made at different values of the temperature of the left hand bulb. The temperature difference between the two bulbs may be taken as a measure of the supersaturation at which growth

occurs. If the temperature difference is plotted against growth rate it is found that the latter decreases linearly with supersaturation (i.e. temperature difference) down to very low supersaturations. There is however a critical supersaturation below which no measurable growth occurs. Volmer and Schultze obtained a value of about 0.8% for the critical supersaturation in this case. They believed that the existence of such a critical supersaturation favoured the adsorption layer theory. However Burton and Cabrera (1949) showed by a quantitative examination of the experimental data that the results actually provided a powerful argument against the classical theory.

(4) BURTON AND CABRERA'S RE-EXAMINATION OF THE CLASSICAL THEORY.

The re-examination of the classical theory by Burton and Cabrera (1949) may be considered in two parts. Firstly the demonstration of the defect of the theory and secondly an examination of the possible errors.

Defect of the classical theory.

Burton and Cabrera attempted to correlate the experimental data of Volmer and Schultze (1931) with the theoretical results expected on the basis of equation (8) on page 21. As will be shown, they found an error of

formidable dimensions.

Volmer and Schultze had observed that when the temperature difference between the arms of the U-tube was 0.15°., the maximum rate of growth was 0.02 mms./hour. This is equivalent to a rate of $0.002 \times 60 \times 60 \times 10^{7}$ layers persecond (assuming a layer thickness of the order of $10A^{\circ}$), i.e. 7.2×10^{7} layers per second.

Now from equation (8) :

$$V_{max} = Z\ s\ e^{-\left(\frac{\phi}{kT}\right)^2 / \ln\alpha}$$

Z may be obtained from kinetic considerations : imagine a one centimetre square on the surface of the crystal. Now if the component of the root mean square velocity of the molecules in a direction perpendicular to the surface is u_x, then half the molecules contained at any instant in a rectangular block of height u_x standing on the square will strike the square in one second. (The molecules have an equal chance of moving towards the square or away from it - the effect of collisions will cancel out.)

$\therefore\ Z = \frac{1}{2} n u_x$, where n is the number of molecules contained in one cubic centimetre of gas.

Now if u_y, u_z are the components of the root mean square velocity in the other two axial directions, then $u_x^2 + u_y^2 + u_z^2 = \bar{u}^2$, where $\bar{u}$ is the root mean square velocity. If there are a large number of

molecules, then on average $u_x = u_y = u_z$ and $u_x^2 = \frac{1}{3}\bar{u}^2$. Thus $u_x = \frac{1}{\sqrt{3}}\bar{u} = \sqrt{\frac{p}{d}}$, where p is the pressure of the gas and d its density.

Taking the density of a hypothetical iodine vapour as 1.13×10^{-2} gms./cc. at 0°C, then at atmospheric pressure:

$$u_x = \sqrt{\frac{76 \times 13.6 \times 981}{1.13 \times 10^{-2}}}$$

$$= \underline{9.47 \times 10^3 \text{ cms./sec.}}$$

This value will not vary ~~much~~ with pressure and we can assume the velocity under the conditions of the experiment to be of the same order.

Assuming iodine vapour behaves as an ideal gas:

$$pv = nkT$$

For iodine vapour at 0°C, $p = 4 \times 10^{-2}$ mms. $= \frac{4 \times 10^{-2}}{760}$ atmos.

$v = 1/1000$ litre, if n = mols/cc

$k = R/N = \frac{0.082}{6 \times 10^{23}}$ litre-atmos.

$$\therefore \quad n = \frac{4 \times 10^{-2} \times 6 \times 10^{23}}{0.082 \times 273 \times 1000 \times 760}$$

$$= \underline{1.41 \times 10^{15}}$$

Now $$Z = \frac{1}{2} n u_x$$

$$= \frac{1}{2} \times 1.41 \times 9.47 \times 10^{18} \text{ mols/cms}^2/\text{sec}$$

$$= \underline{6.68 \times 10^{18} \text{ mols/cms}^2/\text{sec}}$$

For a crystal of millimetric dimensions we may take $s = 10^{-2}$ cms^2.

L_s, the molar heat of sublimation of iodine, has a value of 14.5 k/cals. If we consider only nearest

neighbour interactions, the energy expended in removing one molecule from the lattice is 6ϕ, Thus the molecular heat of sublimation $l_s = 6\phi$.

$$\therefore \phi = \frac{l_s}{6} = \frac{L_s}{6N}$$

$$\therefore \frac{\phi}{kT} = \frac{L_s}{6NkT} = \frac{L_s}{6RT}$$

$$= \frac{14.5 \times 10^3}{6 \times 2 \times 273}$$

$$= \underline{4.4}$$

From the Clausius-Clapeyron equation:

$$\ln \alpha = \ln \frac{p}{p_o} = \frac{L_s \Delta T}{RT^2}$$

$$= \frac{14.5 \times 10^3 \times 0.15}{2 \times 273^2}$$

$$= \underline{1.46 \times 10^{-2}}$$

$$\therefore V_{max} = Z s e^{-\left(\frac{\phi}{kT}\right)^2 / \ln \alpha}$$

$$= 6.68 \times 10^{18} \times 10^{-2} \times e^{-\frac{4.4^2}{1.46 \times 10^{-2}}}$$

$$= 6.68 \times 10^{16} \times e^{-1326}$$

Observed growth rate $= 7.2 \times 10^7$ layers/sec

$$\therefore \frac{\text{Experimental rate}}{\text{Theoretical rate}} = \frac{7.2 \times 10^{-9}}{6.68} e^{1326}$$

$$= \underline{e^{1300}} \quad \text{(approximately)}$$

There is thus an enormous discrepancy between theory and experiment.

Alternatively we may calculate the supersaturation necessary to give a growth rate which is just measurable - say 10^{-3} layers per second (i.e. of the order of

one micron per month):

$$10^{-3} = Z\, s\, e^{-\left(\frac{\phi}{kT}\right)^2 / \ln \alpha}$$

$$= 6.68 \times 10^{16} \times e^{-19.4/\ln \alpha}$$

Taking natural logarithms :

$$\frac{19.4}{\ln \alpha} = 45.7$$

$$\therefore \quad \ln \alpha = \frac{19.4}{45.7} = 0.425$$

$$\therefore \quad \underline{\alpha = 1.53}$$

i.e. a supersaturation of about 50% is theoretically necessary, although Volmer and Schultze estimated the critical supersaturation at about 0.8%.

Examination of Possible Errors.

Burton, Cabrera and Frank (1951) point out that Becker and Döring (1935) neglected configurational entropy: this is equivalent to assuming that the shape of the critical nucleus is always the same as it is at $0^{\circ}K$. In fact the nucleus is not square as assumed but has slightly rounded corners.

If in the calculation of G_c we assume that we have a circular nucleus radius $\underline{l}$, instead of a square edge length $\underline{l}$, then equation (1) becomes :

$$dG = \sigma \times 2\pi l\, dl - \frac{2\pi l^2 dl}{a^2}\, e'$$

and the corrected value for G_c in equation (4) becomes $\frac{\pi \sigma^2 a^2}{e'}$ instead of $\frac{4\sigma^2 a^2}{e'}$. There is thus a reduction of $\pi/4$ or 0.78 in the value of G_c. The actual shape

of the nucleus lies between the two extremes of a square and a circle. Accordingly the correction factor must lie between 0.78 and 1.00. Burton and Cabrera calculate the exact value as 0.86, but even taking the minimum value of 0.78 it is seen that the error introduced by the assumption of a square nucleus is negligible compared with the huge discrepancy involved.

Burton and Cabrera further consider the influence of diffusion on the nucleation process. They show that an error is introduced by neglecting this but once again the magnitude of the error involved is infinitely small in comparison to the defect.

The above workers also consider the results in the light of the theory of kinks. They show that, while a step edge contains about one kink for every four molecules in the step, there is a negligible number of kinks on the surface of a step unless the temperature is near the melting point. Thus the suggestion of Frenkel (1945) that renucleation could be effected by thermal fluctuations of the molecules can be ruled out for growth at normal temperatures.

There thus appears to be no explanation of the defect in terms of the classical theory.

(5) THE FRANK DISLOCATION THEORY.

The re-examination of the classical theory showed no possible method of reconciling theory and experiment. It is therefore fairly obvious that there must be some fundamental error in one of the basic assumptions of the classical theory.

Frank (1949) pointed out that all the classical theories considered growth of perfect crystals in which each lattice point was situated at the ideal distance from its neighbours. However it is known that the tensile strengths of metal crystals are only a small fraction of the theoretical value calculated for a perfect crystal. This fact, taken together with evidence from X-ray diffraction intensities, lead Taylor (1934) and Orowan (1934) to postulate the existence of certain irregularities, or dislocations, in crystals.

The discrepancy between observed and theoretical values of the growth rate can thus be rationalised by considering that crystal growth rate, like tensile strength exhibits anomalous values as a result of the presence of dislocations in crystals.

It has been shown that all irregularities of this kind may be described in terms of two types of dislocation. The first of these, termed edge or line dislocation was described by Taylor (1934) and Orowan (1934). The second type termed screw dislocation was described

by Burgers (1939).

All dislocations can be produced by slip and it is convenient to describe them in terms of slip.

Suppose we have a cubic crystal block as in Fig. 2(a) (page 30) and that we make a cut along the plane ABCD. Now let us suppose that the crystalline material lying above ABCD is compressed so that we have a ledge CDD'C' protruding from the crystal below CD as in Fig. 2(b).

We will consider the case where the vector CC' (called the slip vector) is equal to the lattice unit translational vector. The vector is then said to have undergone unit slip. The material lying above ABCD has slipped but lies adjacent to crystalline material which has not slipped. At the boundary there will be a region over which severe lattice distortion will exist, the atoms not being at the ideal distance from their neighbours. This region is fairly localised and may be considered to be confined to a line AB. This Line AB is called the dislocation line - it is the internal boundary in the crystal of the slipped area. It is seen that for this type of dislocation the slip vector is perpendicular to the dislocation line and this is the definition of an edge dislocation.

The dislocation may also be described in another manner : if we consider the lattice above and

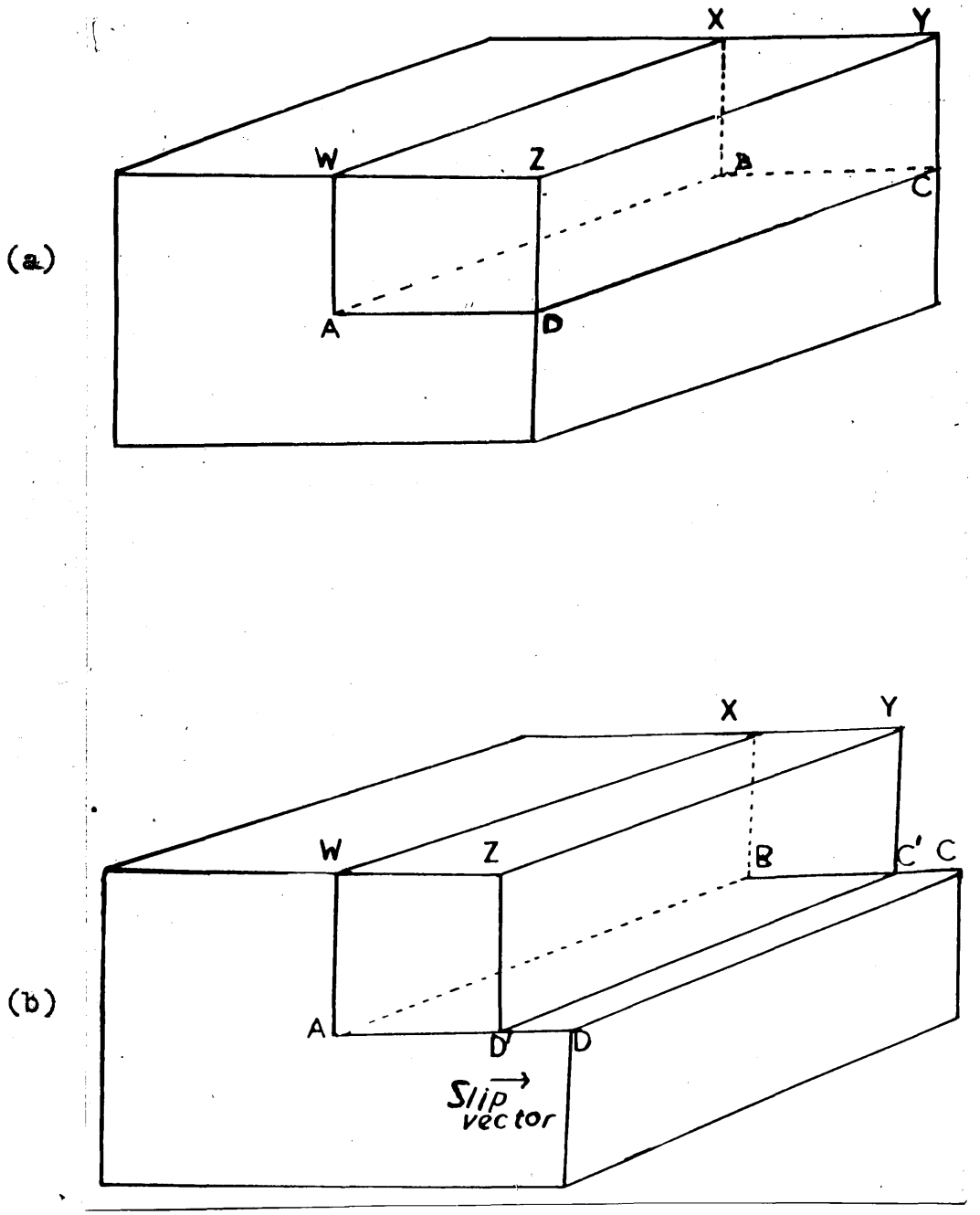

Fig. 2

Formation of an edge dislocation : ABCD is a cut in a cubic crystal (Fig (a)). Slip over this surface as in (b) produces an edge dislocation. The slip vector CC' (or DD') is seen to be normal to the dislocation line AB.

and below AD' it is seen that we have one more atom above than below because of the unit slip (Fig. 3(b), page 32).

Now compare this with a perfect lattice (Fig. 3(a)). The difference is best illustrated by performing a circuit in the two lattices. In this circuit we shall move from a point in the lattice to another point three atoms to the right, then three atoms up, three atoms left and finally three atoms down. If we perform such a circuit PQRSP (called a Burgers circuit) in the perfect lattice (Fig. 3(a)) the starting and finishing points are identical. However, on performing the circuit in the imperfect lattice (Fig. 3(b)), it is seen that the circuit fails to close and we have a vector PP' between the starting and finishing points. This vector is known as the Burgers vector and it it is seen that it is equal to the slip vector in magnitude and direction. Thus an edge dislocation has its Burgers vector perpendicular to the dislocation line.

To produce a screw dislocation in a crystal let us once again imagine a cut ABCD in a cubic block (Fig. 4(a), page 33). This time, however, let us rotate the two halves of the crystal on either side of ABCD so that we have a lip CC' on the upper surface of the crystal (Fig. 4(b)). Let us again suppose that unit slip has occurred so that CC' is equal to the lattice unit translational vector. If BC' was a straight line we should

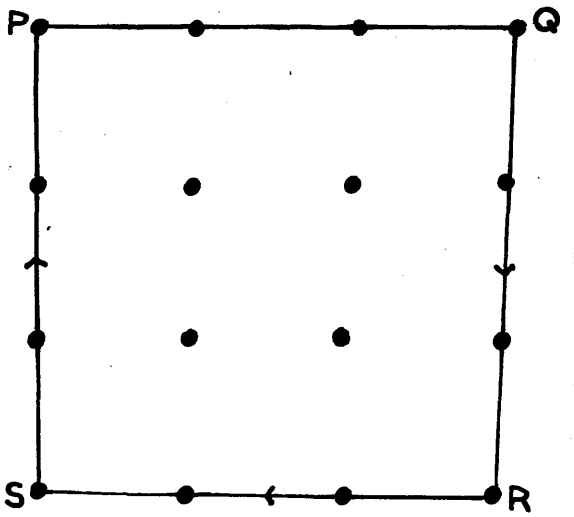

Fig. 3(a)

Burgers circuit in perfect lattice which closes on itself.

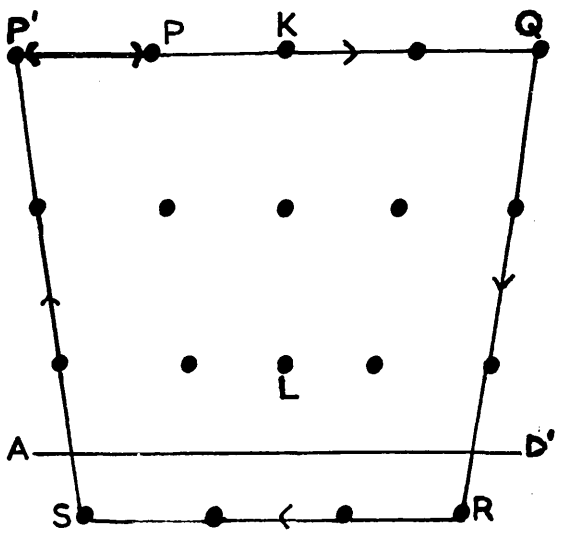

Fig. 3(b)

Burgers circuit in lattice of Fig. 2(b) containing edge dislocation. The circuit fails to close by vector PP' (Burgers vector) which is parallel to the slip vector.

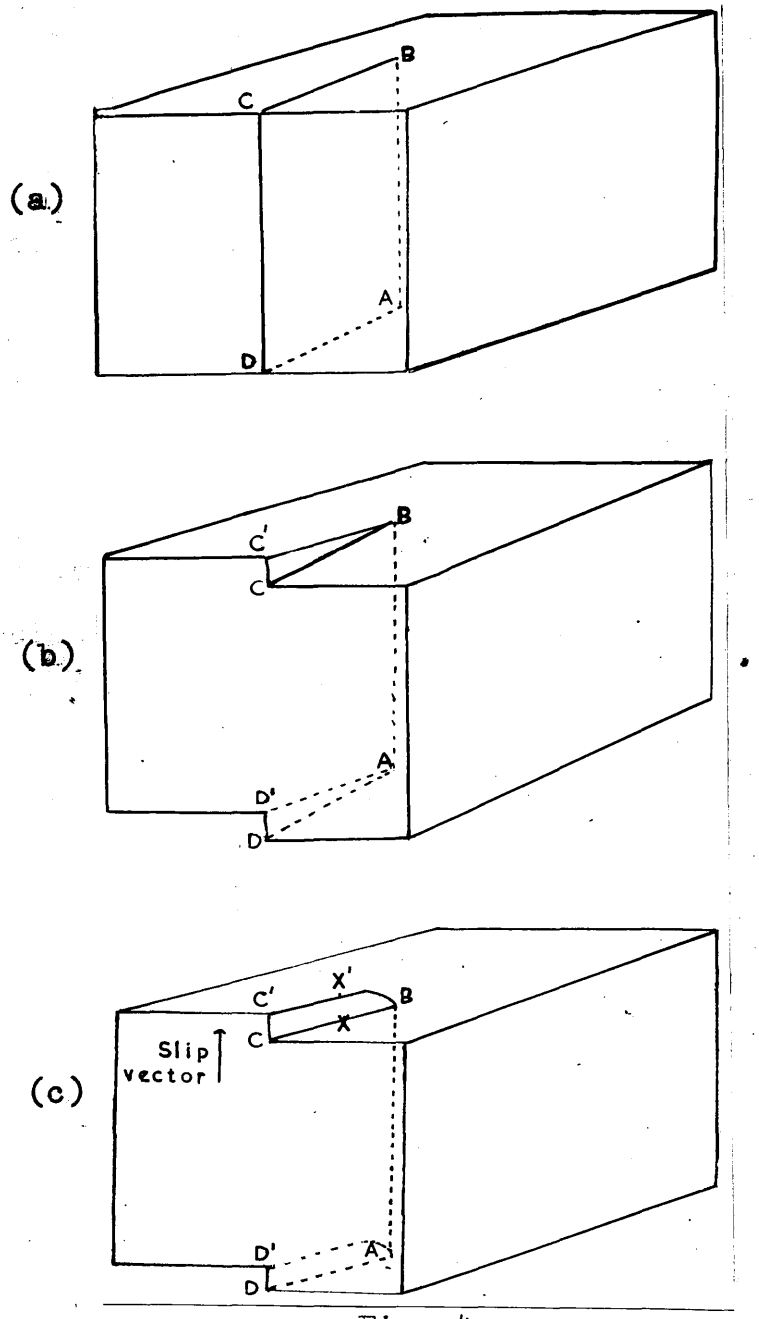

Fig. 4

Production of screw dislocation: two halves of crystal rotated about cut ABCD in (a) to give lip CC' as in (b). This structure involves great distortion and that in (c) is preferred. A Burgers circuit starting at X' finishes at X. The Burgers vector XX' and slip vector CC' are parallel to the dislocation line AB.

have distortion all along ABCD, whereas in fact the distortion is again localised to a region within a few atomic diameters of AB and we have a step BCC' on the crystal surface, whose height may be taken as equal to the unit lattice distance along its entire length (Fig 4(c), page 33). In this case the slip vector is parallel to the dislocation line and this is the definition of a screw dislocation.

Further if we start at X and perform a Burgers circuit it is fairly readily seen that we shall finish at a point X' which originally corresponded to X on the other side of the slip surface ABCD. However X' is now one atomic plane above X so our Burgers vector is XX' and once again this is equal to the slip vector in magnitude and direction.

From the description of the above Burgers circuit it is seen that we have travelled from one atomic plane to the one above without any definite jump. It is thus possible to make a series of Burgers circuits starting at D and to finish at C, moving one plane upwards for each circuit. The atoms can thus be considered to be arranged on a spiral ramp, the dislocation line AB forming the axis of the spiral.

Frank (1949) realised that if such a screw dislocation were present in a growing crystal there would be no necessity for renucleation on completion of an atomic

plane, since the atoms form one continuous ~~plane~~ ramp.

He considered the addition of atoms to a step AB which is produced by the emergence of a screw dislocation at the surface (Fig 5(a), page 36). Since the step is fixed at A, the whole step pivots on this point. Further since the rate of growth is the same at all points along AB (i.e. the linear velocity of points along AB is constant), the angular velocity of the points nearer A must be greater than that of points nearer B. Thus the first stage of the growth is represented in Fig. 5(b). The step AB will eventually wind itself into a spiral as shown in Figs. 5(c) and (d). Since the step is growing outwards all the time, after a few turns an equilibrium shape will be reached.

The spirals shown in Figs. 5(c) and (d) are circular in shape. However, in actual fact, the close-packed planes tend to grow outwards more slowly. Polygonal spirals are therefore formed with straight edges corresponding to the close packed planes as in Fig 5(e). As the close packed planes determine the shape of the crystal, the spirals therefore have the same shape as the crystal itself.

Frank also considered growth from two screw dislocations close together. If these are of the same sense, two intertwined spirals are produced. If, however, they are of opposite sense, then closed loops

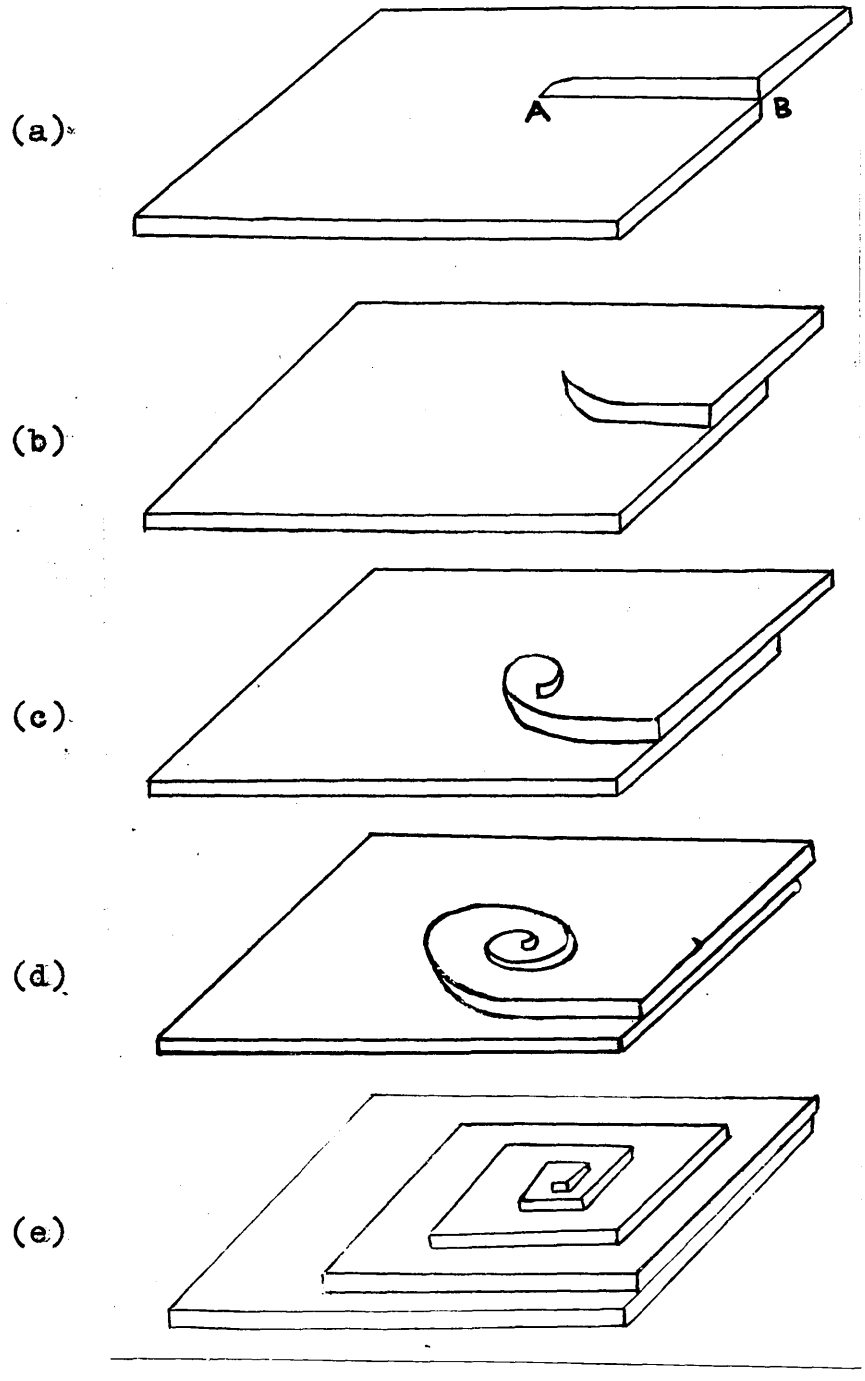

Fig. 5

Stages in formation of spiral by growth on screw dislocation edge in (a). Circular spiral formed in (b) (c) (d). Polygonal spiral results from slow growth of close packed faces (e).

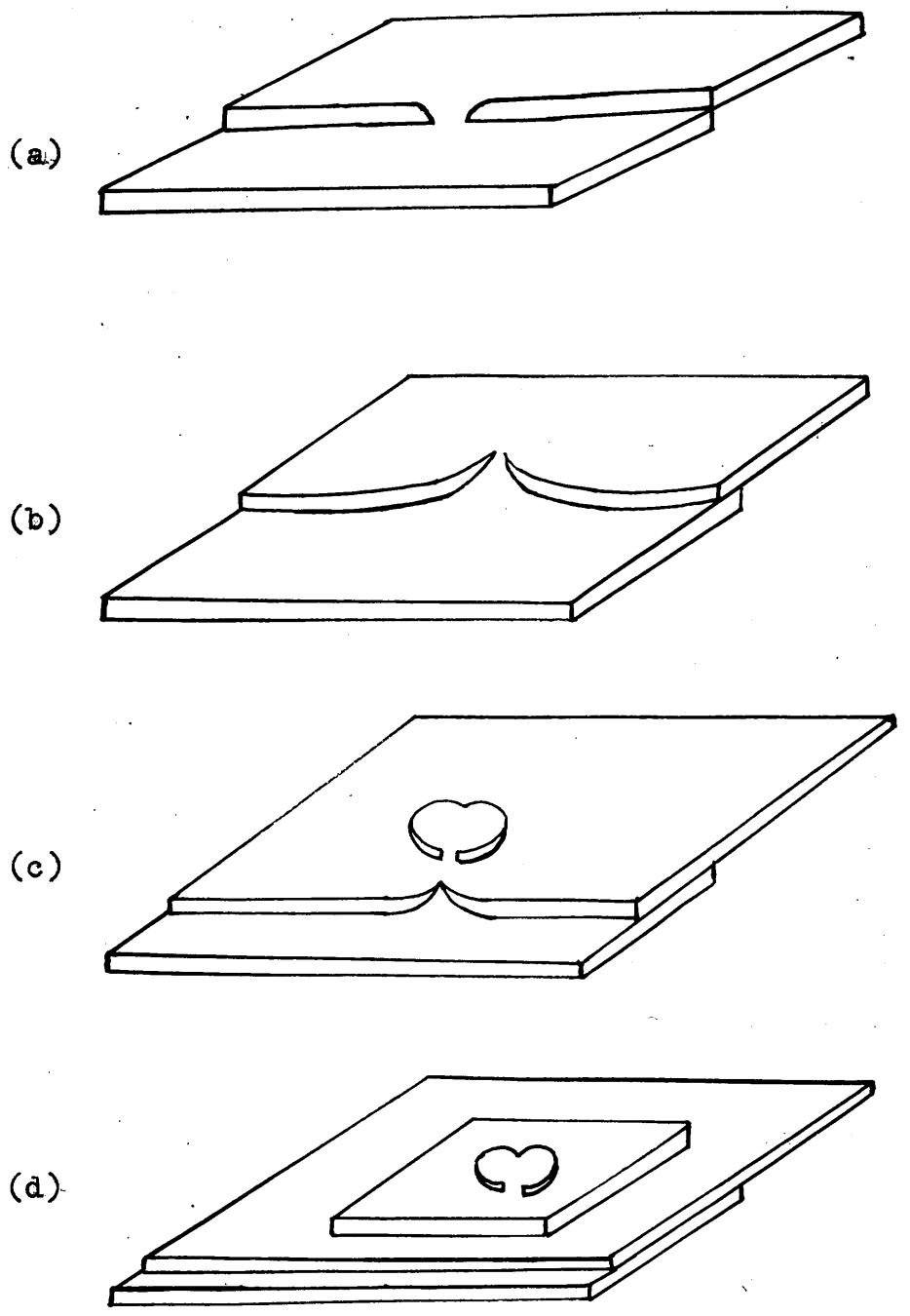

Fig. 6

Stages in formation of closed loops by growth on two dislocation edges of opposite sense as in (a). The two grow independently (b) and then join to produce a step and a half loop (c). Further growth generates closed loops as in (d).

result as shown in Fig. 6 (page 37).

It is seen, therefore, that the theory is based on the failure of the classical theory to account quantitatively for the measurements of Volmer and Schultze and on the existence of imperfections in all crystals.

The theory and some of the experimental evidence in favour of it have been reviewed by Frank (1952).

(6) EXPERIMENTAL CONFIRMATION OF FRANK'S THEORY.

Observation of Spirals.

Frank's theory was soon amply confirmed by evidence adduced from the two methods which have been most used in recent work in this field. Phase contrast studies by Griffin (1949) on beryl crystals demonstrated the existence of razor blade like markings and spirals resulting from growth by the Frank mechanism.

Using the electrom microscope Dawson and Vand (1951) studied artificially grown crystals of the hydrocarbon n-hexatriacontane, $C_{36}H_{74}$, and once again found spiral growth terraces. A striking feature of these observations was that all the patterns theoretically predicted by Frank were encountered.

Since then many workers have found evidence of

spiral growth on a large variety of compounds using light, phase contrast and electron microscopy. These observations are summarised in Table I.

TABLE I.

Compounds on which spiral growth has been observed.

Type	Compound	Worker(s)	Method*	Step height*
(a) Natural crystals				
	Beryl	Griffin(1949)	P	M
	Clay minerals	Dekeyser & Amelinckx(1952)	P	M
	Graphite	Horn(1952)	L	MU
	Pyrite	Seager(1952)	L	MU
	Haematite	Verma(1952a)	P	M
	Quartz	Amelinckx(1952a)	P	MU
		Weill(1952a)	L	MU
		Willis(1952)	L	MU
	Apatite	Amelinckx(1952b,c)	P	M
	Mica	Amelinckx(1952d,e)	P	MU
	Biotite	Amelinckx(1952d,f)	P	M
(b) Experimentally grown crystals				
(1) From vapour.				
(i) Organic compounds				
Aromatic hydrocarbons Benzoic acid Camphor derivatives Diphenyl Phenylacetic acid amines etc.		Brandstätter(1952, 1953)	L	MU

Type	Compound	Worker(s)	Method*	Step ht.*
(ii) Inorganic substances				
	Ice	Mason & Owston (1952)	L	MU
	Carborundum	Verma(1951,1952b,c,d)	P	MU
		Amelinckx(1951a,b,c, 1952g)	P	MU
		Weill(1952b)	P	MU
	Magnesium	Forty(1952b)	L	M
	Silver	Forty & Frank(1953)	L	M
	Cadmium	Forty(1952c)	L	M
	Aluminium boride	Horn, Fullam & Kaspar(1952)	L	MU
(2) From solution.				
(i) Organic compounds				
	Citric acid	Amelinckx(1953a)	P	MU
	n-hexatriacontane	Dawson & Vand(1951)	E	M
	N-nonatriacontane	Anderson & Dawson(1953)	E	M
	N-hectane	Dawson(1952)	E	M
	Stearic acid	Anderson & Dawson(1953)	E	M
		Verma & Reynolds(1953) Reynolds & Verma(1953)	P	M,B,MU
	N-propyl pentacontanoate	Anderson & Dawson (1955)	E	M
	N-hexeicosanol	Amelinckx(1953b,c, 1954)	P	M,B
	Palmitic acid	Verma(1954)	P	M,B,MU

Type	Compound	Worker(s)	Method*	Step ht.*
	Salol	Amelinckx(1952h, 1953a,d)	P	MU
	Thymol	Votava, Amelinckx & Dekeyser(1953)	P	MU
	Behenic acid	Amelinckx(1954)	P	B
(ii) Inorganic substances				
	Cadmium iodide	Forty(1952a)	L	MU
	Lead iodide	Forty(1952a)	L	MU
	Lithium sulphate	Rae & Robinson(1954)	L	MU
⁑	Gold	Amelinckx(1952i)	P	MU
		Amelinckx, Grosjean & Dekeyser(1952)	P	MU
⁑	Platinum	Votava(1953)	P	MU
	Potassium ferrocyanide	Amelinckx & Votava (1953)	L	MU
+	Titanium	Steinberg(1952)	P	MU
(3) From the melt				
	Alumina	Weill (1952a)	L	MU
	Thymol	Votava, Amelinckx & Dekeyser(1953)	P	MU
	Salol	Amelinckx(1953a,d)	P	MU
	Copper	Bethge & Schaffer (1954)	L	MU

⁑Produced by chemical precipitation +Produced by electrolysis

*Abbreviations: P=phase contrast microscopy
L=light microscopy
E=electron microscopy
M=monomolecular, B=bimolecular, MU=multimolecular

It will be seen from Table I that a wide range of compounds of many types, prepared by a variety of methods all show spiral growth terraces.

Step heights and polytypism.

It will be readily seen from the last column of Table I that the step heights observed fall into three main groups, namely monomolecular, bimolecular and multimolecular.

Frank (1951) suggested that the step height was determined by the repeat period in the crystal lattice. Multimolecular steps are explained on the basis of the theory of polytypes. It is well known that if we superimpose two layers of close packed spheres, the molecules in the upper layer fit into the holes in the lower. If a third layer be added the molecules in it will fit into the holes in the second layer. This can be achieved in one of two ways. In the first the molecules are fitted in so that their positions correspond to those of the molecules in the first layer. This packing may be represented ABA. The hexagonal close packed structure is built up by an infinite repetition of this arrangement: ABABAB ---. Alternatively the molecules in the third layer may be fitted into positions different from those of the first layer, in which case the packing is represented by ABC. A repetition of this arrangement ABCABC--- gives the cubic close packed arrangement.

It is possible to build up arrangements differing from these two basic arrangements e.g. ABCACB, ABCACB in which the lattice repeat period is equal to the height of the layer ABCACB. Similarly it is possible to build up larger layers, in which one or two layers of atoms break up the regular arrangement.

In the case of carborundum, the existence of polytypes, as these different arrangements are called, is confirmed by X-ray investigations. Correspondingly the step heights on carborundum crystals have been found to correspond to the lengths of known polytypes (Verma 1951,1952b, c,d, Amelinckx 1951 a,b,c, 1952g). These larger steps are supposed to grow without dissociation because of a hold up in the growth by one molecular layer in the step, (Frank 1951, Cabrera 1953). This slow growing layer may be a rapidly growing layer in another direction, in which the growth is held up by another layer. This will give rise to the phenomenon of cross-lacing in which the spiral steps are "cross-laced" at the corners. This cross-lacing is found on carborundum crystals.

"Cross-lacing" is also exhibited by cadmium iodide crystals and Forty (1952a) has accordingly employed the theory of polytypes to explain the occurrence of very large multimolecular steps on these crystals. No X-ray evidence exists for these very large polytypes but Forty attributes this to the large size (up to 2000A°)

of the polytypes, in which only one or two atoms may be out of place in the multimolecular layer. However smaller polytypes should also occur and there is X-ray evidence for these (Hägg 1948, Mitchell 1954). However none of the polytypes so far detected by X-rays have long axis spacings equal to the step heights observed by Forty.

The main achievement of the polytype theory has been in its explanation of the uniform repetition of the polytypic arrangement throughout the lattice. This will obviously occur as a consequence of the spiral growth on an exposed step possessing the polytypic packing. The structure exposed on this step will be repeated throughout the lattice.

Recently Verma (1954) and Amelinckx (1954) have postulated the existence of polytypism in long chain organic compounds and have explained the existence of multimolecular steps in these compounds on this basis. However there has never been any X-ray evidence for the existence of polytypes in long chain compounds. Amelinckx bases his theory on the occurrence of cross-lacing on the crystals of the alcohol n-hexeicosanol-1, $C_{26}H_{53}OH$. It seems however that cross-lacing need not always indicate polytypism and at present it would appear to be rather precipitate to propose that every compound exhibiting cross-lacing must of necessity be polytypic. Further

although Reynolds and Verma (1953) and Verma (1954) claim that ter- and tetra-molecular steps occur on stearic and palmitic acid crystals, Anderson and Dawson (1953) have never found steps of a height greater than two molecules on stearic acid crystals. Their electron microscope studies did, however, demonstrate the frequent occurrence of "bunching" of steps and this may have lead to the apparent observation of steps of greater height in the interferometric measurements of Verma.

Anderson and Dawson (1953) in contrast to Frank (1951) postulate that step height is determined by the size of the molecular unit present in solution. Thus the hydrocarbons exhibit only monomolecular steps. Stearic acid, on the other hand, exhibits bimolecular steps, since the molecules are associated in solution to give a dimer. It should be pointed out that cadmium iodide solutions possess an anomalous activity and this is attributed to complex formation of an uncertain nature (Stokes 1948). This may have a bearing on the occurrence of multimolecular steps on crystals of this compound. Further, the experiments of Forty (1952) were carried out at supersaturations considerably higher than those employed by Anderson and Dawson (1953). This also applies to the experiments of Brandstätter (1953) which were, in addition, carried out from the vapour phase. The high supersaturation may result in additional effects which will be discussed

later (see "Graf lamellar growth theory" in section (7)).

Origin of dislocations.

Frank (1951) takes the view that dislocations result from buckling of the crystalline lattice due to uneven distribution of impurities. This mechanism was modified by Anderson and Dawson (1955). They have shown from studies on n-propyl pentacontanoate, that dislocations are formed at the edge of the crystal. Assymetric growth of the crystal then results in the eventual situation of the dislocation in the centre. They imagine dislocations are formed by slip at the edge of the crystal and point out that the chains in paraffin crystals can easily slide over one another. They do however make the reservation that the mechanism may differ from this in other compounds.

Cancellation of dislocations.

In their study ofthegrowth of n-nonatriacontane crystals Anderson and Dawson (1953) obtained clear evidence for the cancellation of dislocations by internal slip. The importance of these observations is that the occurrence of flat topped crystals is no longer conclusive evidence that growth has not occurred by the Frank mechanism. Thus any demonstration of the invalidity of the Frank theory will entail production of evidence other than the occurrence of flat topped crystals. Forty and Frank (1953) found no trace of spiral growth on zinc crystals and Anderson

and Dawson (1953) attribute this to "punch-through" resulting in cancellation of the dislocations.

(7) OTHER GROWTH MECHANISMS.

Two other growth mechanisms have been proposed since Frank put forward his theory. Both of these, however, are likely to be complementary, rather than alternative, processes to the Frank mechanism. The two are the twin growth mechanism proposed by Dawson (1952) and the lamellar growth theory of Graf (1951).

Dawson Twin Growth Mechanism.

Evidence for this mechanism was found in the study of n-hectane crystals (Dawson 1952). As well as spirally grown crystals of the normal type, there also occurred long lath like crystals. These crystals although they appeared to have grown vertically by spiral growth, were greatly extended in a lateral direction. Electron diffraction showed that these crystals were twinned. Accordingly Dawson (1952) postulated that they grow by virtue of the fact that the twinned lattice provides a re-entrant edge at which addition of molecules can readily occur. Further additions create a new re-entrant edge. Thus there is an indestructible step at the tip of the twinned crystal which can therefore continue to grow quite rapidly in a lateral direction.

Twin growth has also been observed on crystals of n-do-octacontane (Dawson and Duncan, unpublished work), n-propyl pentacontanoate (Anderson and Dawson 1955) and in mixed paraffin crystals (Anderson and Dawson, unpublished work).

Graf Lamellar Growth Theory.

This theory was introduced to deal with the very rapid growth which occurs at high supersaturations. According to Graf (1951) the crystal nucleus is originally spherical and retains this shape until it reaches a size where its mechanical strength no longer balances the surface tension forces. At this stage all the surfaces will grow out except the closest packed surfaces. On these the potential hollows are too shallow to adsorb the highly mobile molecules arriving at the surface. Accordingly they migrate across the surface of the crystal and condense on the non-close packed surfaces at the edge. Consequently the crystal becomes extended in one direction and needle like crystals result. These crystals will have extremely irregular edges since these edges are not close packed.

A further nucleus may condense on the surface of this crystal and it will go through the same process. Thus a second thick sheet is formed over the first.

This theory is thought to account for the lamellar growth exhibited by metal crystals at high

supersaturations.

Graf proceeds to deduce the crystal shapes expected on the basis of his theory. He does not attempt to relate his work to that of Frank, although there is a distinct possibility that a combination of the two theories might explain the occurrence of multimolecular steps, particularly on crystals such as those of cadmium iodide which were grown by Forty at fairly high supersaturations.

More recently Bethge and Schaffer (1954) have shown that in the growth of copper from the melt, most of the crystals exhibit lamellar growth while only a very few show spiral growth steps.

It does seem apparent then, that in studying growth under conditions of high supersaturation, consideration should be given to the ideas of Graf.

(8) AIMS OF THE PRESENT WORK.

From the work described above, it is self evident that the Frank theory has been shown to apply to a large number of compounds of varying type. Accordingly we may take it that the theory has been vindicated and is at least of fairly general application.

Thus in the present state of the problem a mere examination of crystals to discover growth spirals is no longer of much significance. What is now required is

more detailed information in order that our knowledge of crystal growth processes may become more complete. Further work in this field should therefore be directed firstly, to a more detailed examination of the growth processes in certain compounds, in order that the modifications to the theory necessary in specific cases may be assessed. Secondly, an attempt should be made to determine the range of application of the theory if this should be limited. We thus take the Frank theory as the basis of all work in this field and use it to classify the results for compounds which do not conform exactly.

Under the heading of possible modifications to the theory it should be remembered that the Frank theory in its original form applies to growth from the vapour phase. As Frank (1949) points out the differences in principle between growth from the vapour and from solution are not very great. Nevertheless various solvent effects such as rate of evaporation may be of importance in certain cases. Further if the solute can undergo association the polarity of the solvent may be of importance.

Temperature effects should also be considered in this connection. Anderson and Dawson (1955) have stressed the part played by temperature in the formation of screw dislocations. Also, although Burton, Cabrera and Frank (1951) have shown that surface roughness is of no importance in growth at room temperatures, at temperatures near

the melting point the reverse holds. Thus the study of crystal growth at elevated temperatures will also be of importance in studying possible modifications to the Frank theory.

Further modifications may be necessary in individual cases by virtue of differing molecular shapes and sizes. Frank (1949), Dawson and Vand (1951), Dawson (1952) and Anderson and Dawson (1955) have all pointed out the importance of structural factors. Despite this the information on structural effects on growth is still rather scanty.

The question of structure sensitivity leads us quite naturally to the heading of the range of application of the Frank theory. Anderson and Dawson (1955) suggest that their mechanism for formation of screw dislocations is structure sensitive. It does not seem improbable, therefore that a compound may exist whose structure precludes the formation of screw dislocations. If it forms crystals of any type whatsoever these must grow by another mechanism.

Under this heading we must also consider the inter-relation of the Frank and Graf theories. Suppose we take a compound whose crystals are known to grow by the Frank mechanism at low supersaturations. How do they grow at high supersaturations? There would thus appear to be a profitable field for study in growth of

of crystals at high supersaturations. High temperature studies may also be of importance in this connection.

Thus the general aims of this work are, firstly, the study of modifications necessary to the Frank theory by virtue of solvent, temperature and structure effects; secondly, an attempt to assess the range of application of the Frank theory by studying growth at high supersaturations and elevated temperatures and also by endeavouring to study compounds which will only form screw dislocations with difficulty.

(9) MATERIALS SELECTED.

Bearing these aims in mind the materials selected for study were n-pentacontanol-1, n-hexatriacontane, 1-iodohentriacontane, 4-methyltritriacontane, 4-methyltritriacontanone-26 and 18-keto-n-propyl n-pemtacontanoate. Specimens of all these compounds except n-hexatriacontane were very kindly supplied by Professor E. Stenhagen. Dr. C.W. Bunn very kindly supplied the specimen of n-hexatriacontane.

N-pentacontanol-1, $C_{50}H_{101}OH$

The preparation of this compound is described by Ställberg, Ställberg-Stenhagen and Stenhagen (1952). These workers found the melting point to be 104.5°C and

the long spacing of the lattice 131A° which corresponds to twice the molecular length.

X-ray investigations of various other long chain alcohols by Malkin (1930), Bernal (1932), Marwick (1932), Wilson and Ott (1934), Schoon (1938), Ott (1944), Sano and Kakiuchi (1949) and Witnauer and Swern (1950) have all shown a bimolecular long axis spacing. Malkin (1930) from intensity measurements postulates that this is due to the juxtaposition of hydroxyl groups in the lattice.

This compound was chosen chiefly to test further the hypothesis that step height is dependent on the size of the molecular aggregate present in solution. Anderson and Dawson (1953) found bimolecular steps on crystals of stearic acid which is completely associated in solutions in non-polar solvents. However the alcohols are incompletely associated and it was hoped that the present investigation would provide conclusive evidence on this problem.

The association of the long chain alcohols has been studied by infra-red absorption techniques (Fox and Martin 1940, Kreuzer and Mecke 1941, Hofmann 1943, Smith and Creitz 1951) ; by determination of heats of dilution of the substances (Wolf, Dunken and Merkel 1940) ; by measurement of the dielectric polarisation (Goss 1940, Dunken, Judenberg and Wolf 1941) ; by Raman spectra observations (Rao 1945, Malyshev and Shishkina 1949 and

1950) ; by electrical conductivity measurements (Zeiniger and Mecke 1950) ; by heat capacity measurements (Euchen 1948) ; and by the relaxation effects of Hertzian waves (Klages and Kremnlig 1950). These results are partly summarised by Davies (1946). Measurements on alcohols up to hexadecanol, $C_{16}H_{33}OH$, by the methods outlined above show that in non-polar solvents a polymerisation occurs presumably by formation of a hydrogen bond (or bridge) between the oxygen atoms in neighbouring molecules.

Of the polymolecules thus formed only the monomer and the dimer have a definite existence in the solution, the higher polymers being rather indefinite in size. Kreuzer and Mecke (1941) state that only small quantities of the dimer are present in the solution and that in certain cases the dimer concentration is negligible, there being a preference for the formation of ter- or tetramolecular aggregates. On the other hand Fox and Martin (1940) and Smith and Creitz (1951) postulate the definite existence of the dimer in solution.

The results tend to show that the average association decreases as the length of the carbon chain in the alcohol increases and, indeed, such a decrease is to be expected. Wolf, Dunken and Merkel (1940) have pointed out, however, that owing to the considerable temperature variation of the association it is rather difficult to determine the effect of increasing chain length on the

association. They state that the average association increases with increasing chain length. However the decrease, if any, on passing from one alcohol to the next homologue will become much smaller in the case of the long chain alcohols and it is reasonable to suppose that at room temperature n-pentacontanol-1 will be appreciably associated in non-polar solvents.

As the temperature of a solution of an alcohol is increased the degree of association falls off (Rao 1945, Malyshev and Shishkina 1949 and 1950). The effect becomes more pronounced as the chain length is increased. It is therefore probable that at a temperature of 50-60° only a small proportion of the molecules in a solution of n-pentacontanol-1 will be associated.

In polar solvents the alcohols are not associated, presumably because the alcohol molecules tend to form a hydrogen bond with solvent molecules rather than with other alcohol molecules (Wolf, Dunken and Merkel 1940, Hofmann 1943, Rao 1945).

Since there is an appreciable difference in the size of the structural unit presemt in solution in polar and non-polar solvents, it was decided to study the growth from these two groups of solvents. It was further decided to study the crystals obtained from a hot solution in a non-polar solvent since no polymolecules should exist in such a solution.

The non-polar solvents selected were petroleum ether (b.p. 100-120°), xylene and carbon tetrachloride. Amyl acetate, dioxan, iso-propyl, n-propyl, -butyl, and amyl alcohols were used as polar solvents. This selection was made in order to ensure that as far as possible, effects due to differing rates of evaporation of solvent during crystallisation could be assessed for each of the two series individually.

The long chain alcohols exist in several polymorphic forms and the inter-relation between these is at present far from clear. It would appear that the alcohols containing an even number of carbon atoms crystallise at room temperature in a form with tilted chains (B form), while those with an odd number of carbon atoms crystallise in a vertical chain (A) form (Malkin 1930, Marwick 1932, Piper, Chibnall and Williams 1934, Wilson and Ott 1934, Bernal 1932, Schoon 1938). It is assumed that the even number alcohols are converted to the A form near the melting points. Ställberg, Ställberg-Stenhagen and Stenhagen (1952) have shown however, that although this may hold for the lower members of the series, it certainly does not do so for the higher members (those from n-noneicosanol, $C_{29}H_{59}OH$ upwards). Thus the alcohols with 29 and 31 carbon atoms respectively occur at room temperature as an A form and are converted to a tilted chain (B') form near the melting point.

N-pentacontanol-1, $C_{50}H_{101}OH$, exists in the A form, although a few faint lines corresponding to a second crystalline form are reported.

Bernal (1932) found evidence for a further crystalline form when he obtained crystals approximately hexagonal in shape by cooling a melt of dodecanol, $C_{12}H_{25}OH$. X-ray measurements showed that this form had a hexagonal unit cell with two molecules, which must be arranged on a triad axis with the chains vertical. On slow heating the normal form was obtained.

Ott (1944) also found evidence for the existence of a hexagonal form in alcohols in the "glassy state" (intermediate between the melt and the crystalline form). Further evidence has been obtained from anomalous dielectric constants and specific heats near the melting point (Frosch 1942, Dreyfus-Alain and Dunoyer 1952, Kakiuchi, Sakurai and Suzuki 1950).

Hexagonal forms have been reported for methanol and octanol (Dunoyer 1952) and hexadecanol (Sano and Kakiuchi 1948 and 1949).

N-hexatriacontane ($C_{36}H_{74}$)

The long spacing of this compound as measured by X-ray diffraction on a powder specimen is 47,5A° (Dawson and Vand 1951). The crystal growth of this compound at low supersaturations was studied by Dawson and Vand (1951).

These workers showed that under such conditions the substance grows by the spiral growth mechanism.

This compound was therefore selected as being a suitable one for examination under high supersaturation conditions.

4-methyltritriacontane ($C_{34}H_{70}$ - $CH_3(CH_2)_2CH(CH_3)(CH_2)_{28}CH_3$)

The preparation of this compound is described by Ställberg-Stenhagen and Stenhagen (1948) who found the melting point to be 60.7° C and the long axis spacing 46.3A°. The compound undergoes a transition at about 50° C to a tilted chain form with long axis spacing 42.2A°.

Ställberg-Stenhagen and Stenhagen have found a rapid decrease in the intensities of the high order 00l X-ray reflections. They attribute this to a slight disorder in the direction of the c-axis due to the presence of the methyl group, which also causes a slight elongation of the axis in this direction.

At high temperature the normal chain paraffins give a hexagonal form with rotating chains. The presence of the methyl group apparently prevents free rotation of the chains in this compound.

It does seem very likely, therefore, that the linearity of the chains is disturbed by the side chain. Accordingly it is quite possible that slip to form screw dislocations will only occur with some difficulty in this

compound, which would thus be a suitable one for the investigation of the range of application of the Frank theory.

4-methyltritriacontanone-26 ($C_{34}H_{68}O$ - $CH_3(CH_2)_2CH(CH_3)(CH_2)_{21}$-$CO(CH_2)_6CH_3$)

This compound has a long axis spacing of 45.5A° and its melting point is 65.2°C (Ställberg-Stenhagen and Stenhagen 1948). The long axis spacing corresponds to a vertical chain form. This ketone does not exist in a tilted chain form, although many of the other branched chain ketones do. This is due to the side chain as the normal chain ketones only exist in a vertical chain form.

This compound, like the previous one, was selected because it was anticipated that it would only form screw dislocations with difficulty.

18-keto-n-propyl n-pentacontanoate ($C_{53}H_{104}O_3$- $CH_3(CH_2)_{16}CO$ - $(CH_2)_{31}CO_2C_3H_7$)

The long axis spacing of this compound as measured by Ställberg, Ställberg-Stenhagen and Stenhagen (1952) is 70A°. It was selected in the first instance to provide a check on the effect of the keto group on growth and to thus determine which of the effects observed in the growth of the previous compound could be ascribed to the side chain.

It was found that this compound has a very low solubility in most solvents. It would thus appear to

be a suitable compound for studies on growth at high supersaturation. The solubility of most other compounds is such that crystals grown at high supersaturation are very thick and therefore not particularly suited to electron microscopy. The very low solubility of the compound makes it possible to grow crystals at high supersaturation, which are thin enough for electron microscopy.

1-iodohentriacontane ($C_{31}H_{63}I$)

Ställberg, Ställberg-Stenhagen and Stenhagen (1952) found a long axis spacing of 75.8 A° and a melting point of 72°C for this compound. The long axis spacing corresponds to a bimolecular repeat period. This is rather extraordinary as there appears to be no reason why the molecules should pack with the iodine atoms together. Of the other iodides studied by the above workers, those containing 41 and 50 carbon atoms possess a monomolecular repeat period, while that containing 29 carbon atoms exhibits a bimolecular repeat period.

This compound was selected to study the effects caused by a large end group and to discover how far these resemble the effects produced by a branched chain.

1-iodohentetracontane ($C_{41}H_{83}I$)

Ställberg, Ställberg-Stenhagen and Stenhagen (1952) find a melting point of 84°C and a long axis spacing of 49A°for this compound.

The selection of this compound was governed by the desirability of an investigation of the difference in repeat period of this compound from the previous one. It was hoped that the phenomenon might be related to the growth mechanism.

Thus the selection of compounds for study would appear to give a reasonable chance of obtaining further information under the two headings of the previous section, namely the investigation of possible modifications to the Frank theory and its range of application.

III - EXPERIMENTAL

III - EXPERIMENTAL

(1) THE EXPERIMENTAL TECHNIQUES.

Methods of electron microscopy.

The methods available for the electron microscopy of crystals are direct transmission, silicon monoxide replication and pseudo-replication. Of these the first is far superior but it requires crystals which are stable to the electron beam. The stability of a crystal in the beam depends primarily on the melting point and in general crystals with a melting point of less than 50°C are unsuitable for transmission microscopy. However the chemical nature of the compound also seems to be of importance in this connection. Thus some high melting aromatic hydrocarbons undergo decomposition more readily than some lower melting paraffin hydrocarbons. Further it is necessary that the crystals be fairly thin. Thick crystals lead to an enhanced electron scattering and thus to a greater energy release during irradiation. There is thus a greater chance of melting taking place.

Further, in crystal growth studies we are concerned with the observation of surface structures. This is most successfully accomplished when the scattering of the shadowcast layer is high compared to that of the crystal itself. This condition is fulfilled when the crystals are thin.

The silicon monoxide replica method is of use in studying thick crystals but cannot generally be applied to very low melting crystals. For such crystals the pseudo- or formvar replica technique is the only available method.

The techniques of electron microscopy of crystals have been reviewed by Dawson (1953).

(a) Direct Transmission Microscopy.

In this method the crystals are prepared on a thin formvar film supported on Philips or RCA type specimen mounts. The film is prepared by flooding the glass slide with a solution of formvar in ethylene dichloride, floating the resulting film off on water and superimposing it on the specimen mounts. A ½% solution of the plastic was found to give a film of suitable thickness. The ethylene dichloride should be dried by distillation over phosphorus pentoxide before use, otherwise holes tend to be produced in the film.

A drop of solution of the substance under examination is placed on the supported film and the crystals produced by evaporation. A suitable concentration is found by trial and error. Trial crystallisations are carried out on a glass slide and the resulting crystals examined in the optical microscope. Crystals showing edge diffraction effects are generally too thick and a more dilute solution should be used. In performing

tests on substances such as methyltritriacontane and the iodides, which only crystallise with difficulty, it was found advisable to use a slide covered with formvar for the test since solutions giving good results on a glass surface do not necessarily do so on a formvar surface.

When RCA grids were used it was generally found advisable to carry out the crystallisation before floating the film off the slide. The disadvantage of this technique is that when solvents such as petroleum ether are used, the drop of solution spreads over such a large area of the slide that frequently only a monolayer of material is deposited. This may be overcome by adding a small amount of a more viscous solvent such as butyl alcohol to the solution. However care must be taken in the application of this method : it must not be used if the "thickening" solvent is likely to upset association equilibria in solution. Thus, in general, the method should only be applied to substances whose molecules do not possess polar end groups.

If the solution of the substance evaporates too rapidly irregular crystals result. When rapidly evaporating solvents were employed, the rate of evaporation was reduced by maintaining a reservoir of solvent in the dish in which the crystallisation was performed.

In this method the specimens now only require to be shadowcast before examination in the electron microscope.

The shadowcasting process is described in section (2).

In direct microscopy of crystals it is essential that the filament voltage be increased slowly so that no melting of the crystals results from a rapid heating of the specimen. For the same reason the condenser should not be focussed too strongly. It is also advisable for the specimen to make good thermal contact with the holder to facilitate dispersion of excess heat.

In certain cases the solvent may partially or completely dissolve the formvar film. When a solvent such as alcohol is used, the film partly dissolves and the reprecipitation of the film in fibrous form occasionally gives rise to artefacts. Great care therefore has to be taken in interpreting the micrographs in these cases.

If the film completely dissolves in the solvent used, collodion or silicon monoxide films may be used. The latter are prepared by evaporating a thin film of silicon monoxide on to formvar films supported on specimen mounts and then extracting the formvar with ethylene dichloride. Collodion films are not very satisfactory as it is difficult to prepare thin films which are sufficiently strong.

In some cases it was found that there was appreciable contamination of the specimens with dirt. This can be eliminated by preparing a saturated solution of

of the substance at 50°C, cooling and centrifuging. The material which crystallises on cooling carries most of the dirt with it. After centrifuging the clear solution above may be withdrawn with a Pasteur pipette.

(b) Silicon monoxide replication.

This method is the standard alternative when direct transmission is unsuitable. It was first used by Hall (1950) in a study of edestin crystals.

The specimens are prepared as for direct microscopy and shadowcast as before. A thin film of silicon monoxide is then evaporated on to them. This is done by supporting the specimens (in vacuo) horizontally over a molybdenum boat, containing silicon monoxide, which can be heated electrically.

The disadvantage of the method is that a great deal of heat is radiated. Further, measurements with a thermocouple have shown that the condensation of the silicon monoxide on the specimens releases a fairly large quantity of heat. It is found in practice that the best results are achieved with a slow evaporation of 0.1 - 0.2 milligrams of silicon monoxide, the specimens being supported at a distance of 10 centimetres from the boat. The optimum weight of monoxide appears to depend on the exact nature of the surface examined.

Finally, the formvar film and the crystals are

extracted with a solvent which dissolves both. This can be done by introducing a drop of solvent below the mounts, but this frequently results in ruptnre of the replica. The best method is to support the specimens in the reflux vapour of the solvent. However care must be taken not to prolong the extraction, otherwise the replica is again ruptured.

Care must be taken in interpreting micrographs of these replicas, since artefacts may be produced by the melting of the crystals in the replication process.

(c) Pseudo-replication.

This method was first described by Mahl (1940). It was later employed by Zworykin and Ramberg (1941), Schaefer and Harker (1942) and Mahl and Duffek (1942-3). Williams and Wyckoff (1946) improved the method and applied it to the study of virus crystals. These authors used nitrocellulose films for the replicas. In the present work formvar films were used as described by Cosslett (1951).

The crystals are prepared on a carefully cleaned glass slide which is then shadowcast with gold (LePoole 1943). The slide is covered with a formvar film which is then stripped off the slide and supported on specimen mounts as before. The shadowcast layer adheres to the film but the crystals remain on the slide, so that a

shadowcast replica of the surface is obtained.

The technique cannot be used if the crystals are soluble in ethylene dichloride. The metallic layer is usually inadequate for the protectiom of the crystals from solvent action. If the crystals are only partly soluble in ethylene dichloride a replica is obtained which will give largely false information.

The main defect of the method is that some of the metallic layer occasionally adheres to the crystals, leading to parts of the replica being unshadowed. It was found that gold adhered to the replica better than palladium or nickel-palladium.

A further unsatisfactory feature is the presence of tears in the replica as a result of the stripping process. Large tears are easily distinguishable, but smaller tears may lead to misinterpretatiom of the micrographs.

In general this method suffers from so many defects that it should only be employed where all other techniques have failed.

(2) SHADOWCASTING.

When this work was commenced it was decided that an improvement in shadowcasting technique was necessary. In previous work in this field specimens were shadowcast with gold (~~LePoole 1943~~) or palladium (Williams and Wyckoff 1946). The metal was evaporated from a tungsten filament in vacuo, the specimens being inclined at an angle of 15° to the beam of vaporised metal.

It is found however that palladium and, even more so, gold tend to granulate on the surface of paraffin crystals (Plate I, page 70). This results in appreciable loss of resolution. This granulation is not to be confused with the overall granulation resulting on specimens which have been overheated in the electron beam or shadowcast at too high a pressure. The granulation considered here is confined to the surface of the crystals. It appears to be due to a migration of the metal atoms over the crystal surface in the shadowcasting process itself.

An investigation was therefore carried out to discover a shadowcasting metal which gave better results than palladium in the shadowcasting of paraffin crystals.

The use of nickel and palladium in equal proportions was found to yield satisfactory results as shown in Plate II (page 70). The magnification of this picture is several times greater than in the previous one, yet the grain is no worse. Indeed it is concluded that most of

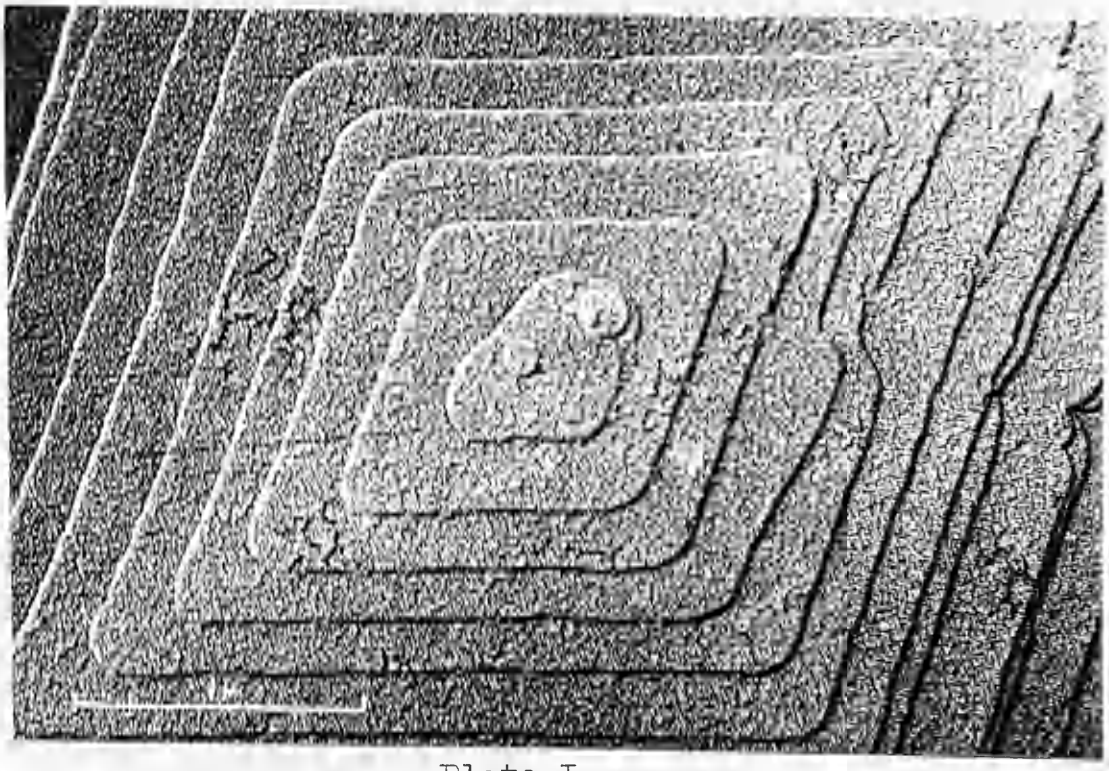

Plate I

This crystal of n-hexatriacontane shows the surface granulation which results on crystals shadowcast with palladium.

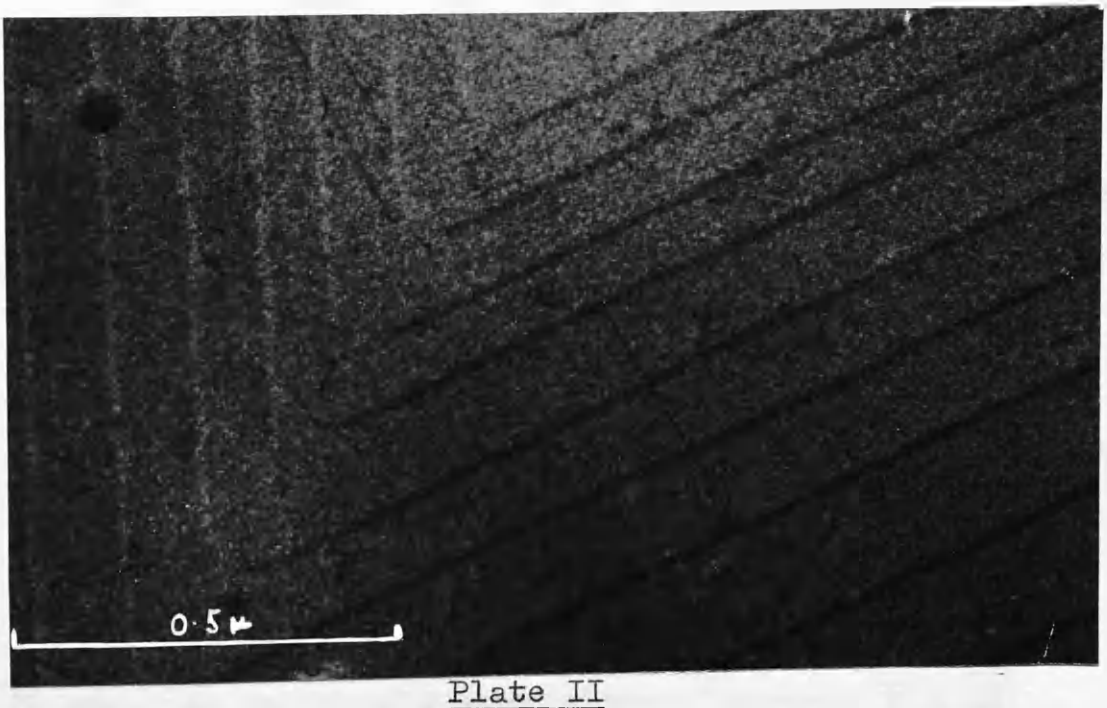

Plate II

This n-hexatriacontane crystal has been shadowcast with nickel-palladium. Despite the greater magnification the grain is no worse than in Plate I. It is thought that most of the residual grain is photographic (see Pl. III,IV)

the residual grain is photographic. This is demonstrated in Plates IV and III (page 72). Both of these micrographs are of the same field at the same magnification. However Plate IV has been subjected to twice the photographic enlargement of Plate III (Plate III was taken at an original microscope magnification equal to twice that of Plate IV). Correspondingly the grain in Plate IV is much worse than that in Plate III, although if the grain was due to shadowcasting it would obviously be the same in both instances.

At first sight it would appear that the efficiency of the nickel-palladium does not depend on an alloy effect since the nickel evaporates first in the shadowcasting. Indeed the grain effect is equally good if the specimens are first shadowcast with nickel and then with palladium. The smaller nickel atoms appear to form a uniform layer over the crystals, which acts as a base for the palladium layer. The use of nickel here would thus seem to be related to its function in electroplating. However since appreciable surface migration of metal atoms will occur on the crystal surface when the metal atoms condense it is possible that an alloy effect may after all be responsible for the efficiency of the process.

The ideal amount of metal to be used was found by carrying out trials with varying amounts. A piece of filter paper was placed beneath the filament in each

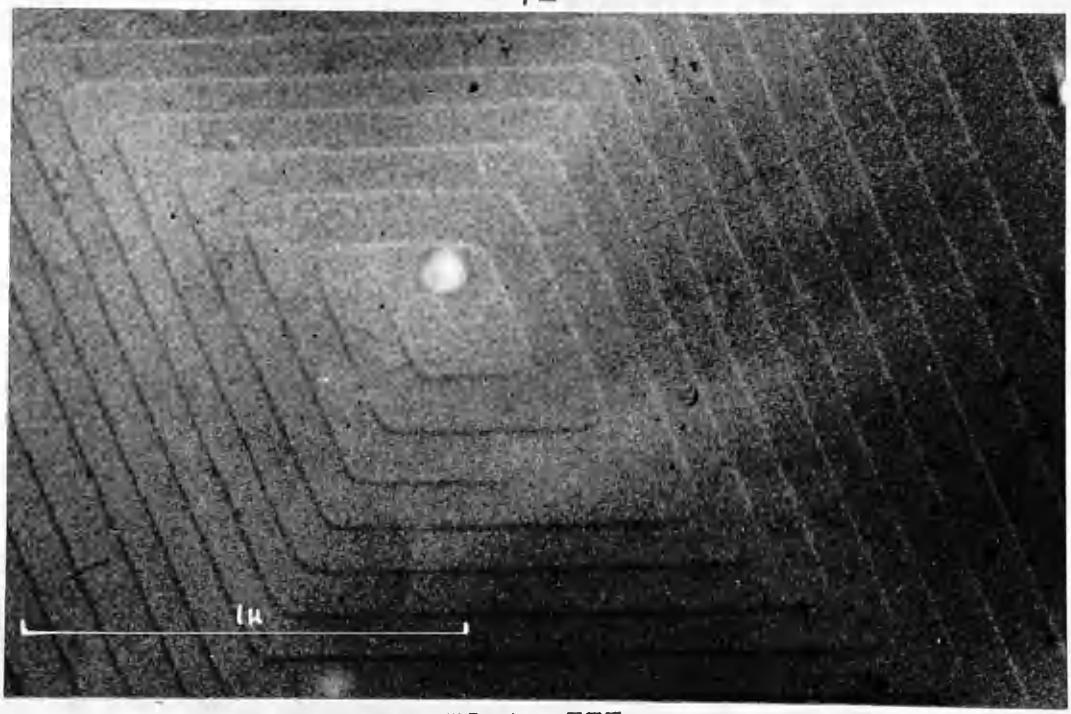

Plate III

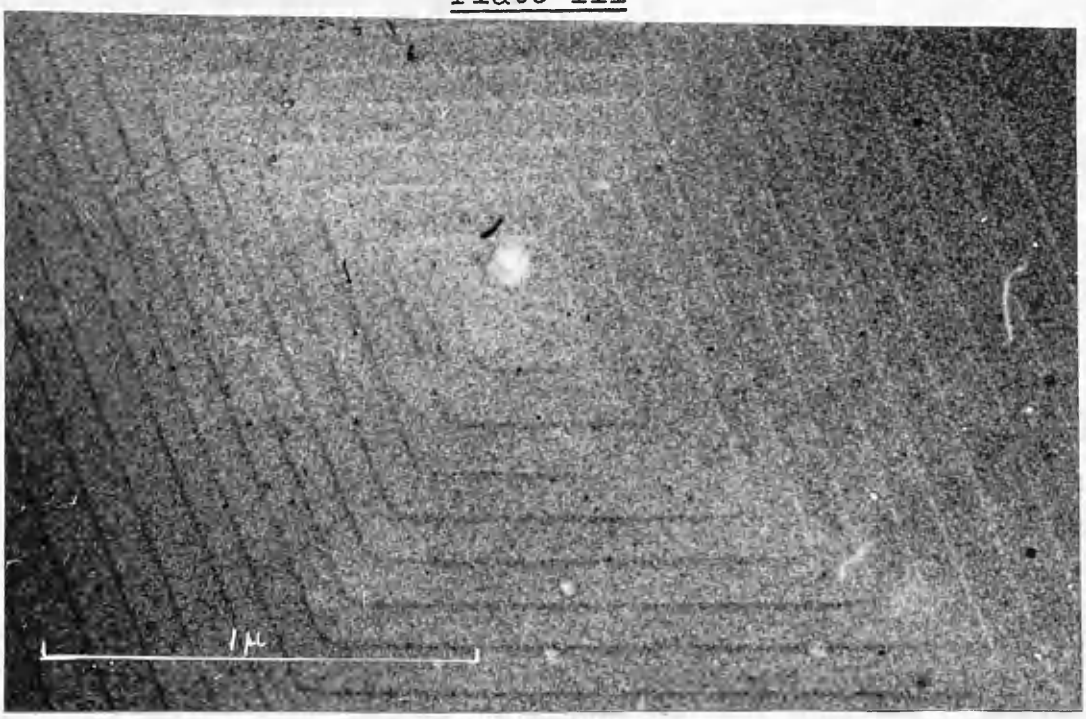

Plate IV

These micrographs show the same crystal (Ni-Pd shadowed) at approximately the same magnification. Plate IV has been subjected to twice the photographic enlargement of Plate III (i.e. original negative of Plate III was taken at twice the microscope magnification of Plate IV). Since the grain is correspondingly far worse in Plate IV it is concluded that most of the residual grain in Ni-Pd shadowed specimens is photographic.

case and the filter paper used in the experiment which gave the best results was retained. In subsequent experiments evaporation of metal was continued until the piece of filter paper beneath the filament was as black as the standard piece. The use of too much nickel has to be avoided, otherwise the sharpness of the shadows is impaired.

The distance of the specimens from the filament was also varied. The best results were achieved when the distance was 25 centimetres.

The shadowcasting should be carried out at a pressure of 10^{-5} millimetres or less. Shadowing at higher pressures results in granulation owing to a decrease in the mean free path of the molecules. It was found advisable to continue pumping for 1-2 hours after the gauge first registered the required pressure. This results in the complete degassing of the filament. If this degassing is not achieved, then there is a release of gas when the filament is heated. The attendant increase in pressure may result in granulation in the shadowcast layer.

Finally it must be emphasised that even if a fine grain is obtained using nickel-palladium shadowing at low pressure, excessive heating when the specimen is examined in the microscope will lead to overall granulation.

The higher resolution attained as a result of the installation of a short focus objective in the electron microscope, has rendered a further improvement in shadowcasting desirable. The higher resolution has facilitated the detection of fine surface structures on crystals of the iodides and branched chain compounds. It is certain, however, that this would have been impossible using the earlier techniques for the shadowcasting of crystals.

(3) COMPARISON OF METHODS FOR CRYSTAL GROWTH STUDIES.

At this point it is of value to consider the relative merits of the experimental methods which are available for the investigation of crystal surfaces.

The two principal methods are electron microscopy and phase contrast microscopy. The latter is usually used in conjunction with interferometric methods for measurement of growth step height. Studies with the optical microscope are of value in certain cases but suffer from the grave disadvantage that they only yield information on coarse surface structure. Such information may lead to serious misinterpretation of surface topography.

The resolution of the Philips electron microscope (fitted with a 25A lens) is 25A° for most purposes. If the specimens are shadowcast it is therefore possible to detect growth features of the order of 10A° in size. The electron microscope thus has a vertical resolution of 10A° and a horizontal resolution of 25A° for shadowcast specimens. It is thus impossible to study crystals with a long axial spacing of less than 10A°. Studies of such crystals would not yield information on the molecular scale desirable for crystal growth work. This severely limits the range of compounds to which electron microscopy may be applied. So far only long chain compounds have been extensively studied, although prelimnary investigations have been carried out on some aromatic hydrocarbons(Anderson and Dawson 1952, unpublished work).

The optical methods depend on interference phenomena between light rays which have a path difference owing to differing thicknesses of a crystal over its surface. The method will thus give a greater vertical resolution than the electron microscope. Amelinckx (1951b,c) has used the method to detect and measure 7A° steps on silicon carbide crystals. However the resolution in the horizontal direction is of the order of the resolution of the optical microscope (i.e.2000A°) and thus closely bunched steps may not be resolved,

although they may be detected by a gradual shift in the Fizeau fringes over an area of the crystal surface. The methods of phase contrast and interferometry are reviewed more fully by Verma (1953).

Step height measurements using interferometry are usually more accurate than those obtained from electron microscopy. This is due to the impossibility of exactly determining the shadowing angle. However as it is usually only required to determine whether a step is one, two, three ---- molecules high, the methods of electron microscopy are quite adequate for the purpose.

Thus electron microscopy would appear to be the more powerful method in view of its high resolution in all directions. However the description of techniques above is sufficient to show that specimen preparation can be very difficult and indeed almost impossible in certain cases. For this reason the two methods are best regarded as complementary and certainly the history of crystal growth investigations shows that considerable advances have been made using both methods.

(4) SPECIMEN PREPARATION.

The methods used in the preparation of specimens in individual cases will be indicated here. Details will be given of any modifications introduced to the standard techniques in particular instances.

(a) N-pentacontanol-1.

The crystals obtained from solutions in petroleum ether (b.p. 100-120°), carbon tetrachloride, xylene, amyl acetate, dioxan, iso-propyl, n-butyl, n-propyl and n-amyl alcohols were studied by the direct transmission method. The method for reducing the rate of evaporation was employed with the first two solvents. The specimens were shadowcast with nickel-palladium. Formvar films were used for all the solvents, with the exception of dioxan, for which silicon monoxide films were employed.

The crystallisation from aqueous alcohol solvents was investigated in the same way, varying amounts of water being used and a batch of crystals being prepared after each addition of water.

It was found that n-propyl and iso-propyl alcohols as normally obtained contained an appreciable quantity of water. It was therefore decided to examine crystals grown from a solution in dried n-propyl alcohol. The solvent was dried by distillation over calcium hydride. Since dry n-propyl alcohol is extremely hygroscopic precautions had to be taken in handling it. The solvent

was kept in tubes stoppered with phosphorus pentoxide and the crystallisation was carried out in Petrie dishes containing phosphorus pentoxide. Prior to crystallisation the dishes (containing phosphorus pentoxide) were heated to 60° and cooled inadesiccator.

Since iso-propyl alcohol is only dried with extreme difficulty, the crystallisation from dry iso-propyl alcohol was not studied.

A crystallisation from xylene at 90-100° was performed on a glass slide heated on a steam bath. The resultant crystals were studied using the method of pseudo-replicas.

The crystallisation from xylene at 40°, 50°, 60°, and 90° was also studied using a closed system for crystallisation. A glass slide coated with a formvar film was placed in a desiccator and heated in an oven at the required temperature for about an hour. The solution was similarly heated and then a few drops were deposited on the slide. The rate of evaporation was reduced by maintaining a xylene reservoir in the desiccator. This was done in order that the second order temperature effect of rapid crystallisation could be separated from the pure temperature effect. The film was then floated off in water and placed over RCA mounts which were shadowcast and examined as before. (The crystallisation at 90°was actually studied by the method of pseudo-

replication since difficulty was experienced in floating off formvar films which had been heated to 90°.) It was hoped that these experiments would yield a direct comparison between a controlled and uncontrolled evaporation at 90°.

(b) 4-methyltritriacontane.

The crystals of this compound were studied by direct transmission microscopy. The method of preparation was by growth on formvar film spread on a glass slide. Solutions in petroleum ether (b.p. 100-120°) were used, a small amount of butyl alcohol being added to check the spread of the solvent as described in section 1(a). The films were deposited on RCA mounts, shadowcast and examined in the microscope.

The crystallisation at 55° was also studied by similar methods to those detailed above for the high temperature crystallisation of n-pentacontanol-1. (The method of controlled evaporation was used.)

(c) 4-methyltritriacontanone-26.

This compound was crystallised from xylene solution and the specimens prepared as in section 4(b) above. The crystals were then studied using the silicon monoxide replica technique described in section 1(b). Ether was used to extract the crystals and formvar film.

(d) 18-keto-n-propyl n-pentacontanoate.

This compound was studied using the same methods as in section 4(b). The crystallisations from petroleum ether, xylene and amyl acetate were studied. A crystallisation was also carried out on films supported on Philips specimen mounts.

A supersaturated solution was prepared and crystallisation initiated. A drop of the solution containing crystals was deposited on a film supported on glass and the excess liquid rapidly blotted off with filter paper, leaving some of the crystals grown at high supersaturation. The film was floated off and deposited on RCA mounts, the specimens shadowcast and examined as before.

(e) 1-iodohentriacontane.

Crystals were prepared from petroleum ether solution on a film spread on a glass slide. A little butyl alcohol was added as before. The preparation of the specimens was exactly the same as under 4(b).

(f) 1-iodohentetracontane.

The preparation of specimens was as described in section 4(b), except that it was found that good crystals were obtained without adding butyl alcohol to the solution.

(g) N-hexatriacontane (high supersaturation).

An attempt was made to grow crystals at a fixed supersaturation. The apparatus shown in Fig. 7 was used. The apparatus was filled with water to a level above the side arm, B. A 0.5 centimetre layer of supersaturated solution in benzene was carefully introduced into the vertical arm, A, some specimen mounts covered with formvar films being allowed to float at the interface. Crystallisation was initiated by scraping the sides of the tube. Crystals were allowed to float down on to the films for a given time and then the mounts were pushed through the water and caught on a silver grid soldered to a copper rod, C. This was introduced through the side arm and withdrawn with the mounts. In this way it was hoped that crystals grown at a fixed supersaturation would be obtained uncontaminated with traces of the mother liquor.

Tests were carried out using unsaturated solutions. It was found that a little material was obtained on some of the mounts thus showing that mother liquor is carried through in some cases. A trace of wetting agent at the interface tended to reduce the amount so transported. Most of the mother liquor remaining on the mounts could now be removed by spraying the mounts with a mixture of acetic acid and a little benzene and withdrawing the excess solution with a Pasteur pipette.

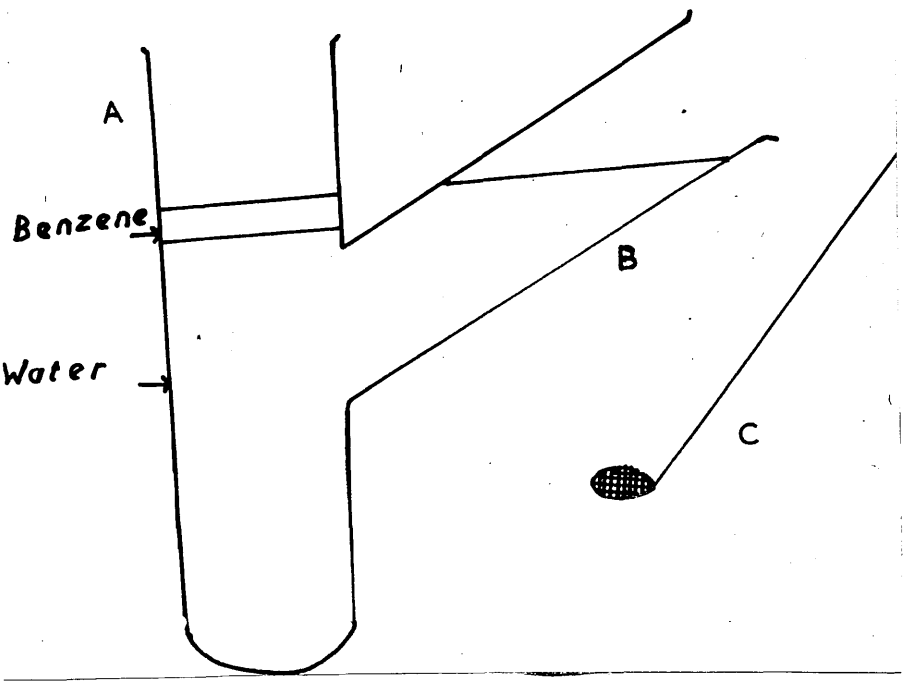

Fig. 7

Diagrammatic representation of apparatus used in supersaturation experiments. The benzene layer contains dissolved hydrocarbon. Specimen mounts are allowed to float at the interface in A. The rod and gauze (C) is introduced through B and the mounts pushed down on to it. They are then withdrawn through B.

The substance is insoluble in acetic acid and the small amount of benzene used will not give any appreciable recrystallisation effect. On the other hand care had to be taken to ensure that the acetic acid did not precipitate material from the mother liquor. Tests were again carried out using unsaturated benzene solutions and it was found that no precipitation occurred provided excessive amounts of the washing solution were not used.

As a considerable number of the films were ruptured in the process, the tube had to be emptied and the process repeated several times to obtain a reasonable number of specimens. The solution was extracted and the hexatriacontane recovered each time.

The apparatus is immersed in a thermostat at 27° as the solubility gradient of hexatriacontane in benzene is fairly steep.

The solubility of hexatriacontane in benzene at 27° was measured as a prelimnary to the experiment. An approximate method was deemed sufficient. The volume of benzene necessary to dissolve a certain weight of the substance was measured by adding the solvent from a microburette to the solid contained in a boiling tube immersed in a thermostat at 27°. The solution was stirred with a copper rod and the point at which all the compound had dissolved determined with the aid of a magnifying glass. (A glass rod was not used as it tended to produce glass

shavings which were confused with hexatriacontane crystals.) Successive determinations gave values of 0.0018, 0.0020 and 0.0019 gms./ml. The approximate value of 0.002 gms./ml. was considered to be sufficiently accurate for the purpose of these experiments.

Using this value solutions of 50% and 100% supersaturation were prepared by warming a weighed quantity of the hydrocarbon with the calculated volume of benzene. The solution was cooled rapidly by immersion in the thermostat before being carefully introduced into the tube as described above.

The time of exposure of the mounts at the interface was varied. It was found that the best results were obtained with exposures of the order of 15-25 seconds for the 100% supersaturated solution and of 30-45 seconds for the 50% supersaturated solution.

The specimens were shadowcast and examined as before.

IV - RESULTS

IV - RESULTS

(1) N-PENTACONTANOL-1.

This section has been divided into (a) a description of the experimental results and (b) a statistical analysis of the results.

(a) DESCRIPTION OF EXPERIMENTAL RESULTS.

The step height measurements described in this section are summarised in Table II (at the end of the section). Table III gives a more detailed analysis of the results, while Table IV tabulates the results of step height measurements at higher temperatures.

Step heights given below are the mean values of a number of measurements. The limits given after each value indicate the mean deviation of the measurements from the mean. Normally at least two step height measurements were made on each crystal : one on a step near the centre and one on a peripheral step. In addition if the shadowing direction was approximately equally inclined to two edges of the crystal, measurements were made on steps on each edge. In the following pages both the number of measurements made and the number of crystals studied are clearly indicated for each step height result quoted.

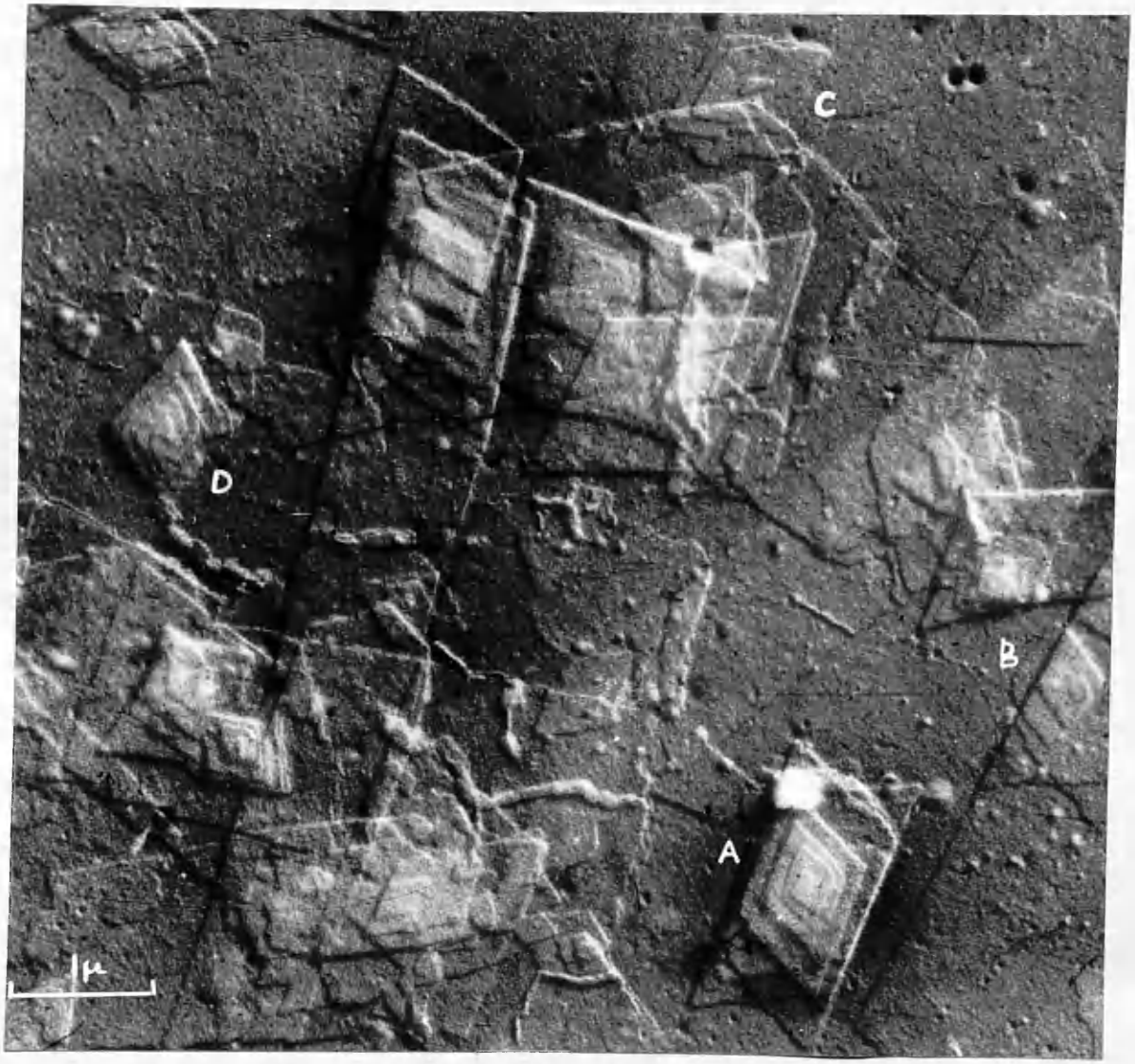

Plate V

This micrograph shows the irregular growth of n-pentacontanol from petroleum ether. Twin laths occur as well as monomolecular (crystals A and D) and bimolecular steps (crystals B and C).

Crystallisation from petroleum ether.

The crystallisation from petroleum ether is in general irregular (Plate V, page 86). Long lath like crystals are formed, these apparently growing by the twin growth mechanism proposed by Dawson (1952). A typical example of such a twin is shown in Plate VI (page 88). Spiral growth terraces can be seen at various points along the laths in Plate V. There are also a few crystals independent of laths which grow by the spiral mechanism (Plate VII, page 88).

The heights of the growth steps fall into two classes. Most of the steps have a height of 69±7A° (mean of 60 measurements made on 24 crystals), but a few have a height of 133 ± 7A° (mean of 16 measurements made on 7 crystals). Of the crystals shown in Plate V, the steps on A are of the first type, while those on B and C are of the second type. On D there are three spirals of the first type.

By comparison with the value of 131A° obtained by Ställberg, Ställberg-Stenhagen and Stenhagen (1952) for the long axis spacing, it is obvious that the two types of step are respectively mono- and bi-molecular.

The steps on the crystal in Plate VII are monomolecular but at the edge bimolecular steps have been formed by the coalition of monomolecular steps. The bimolecular steps have a much straighter edge than the

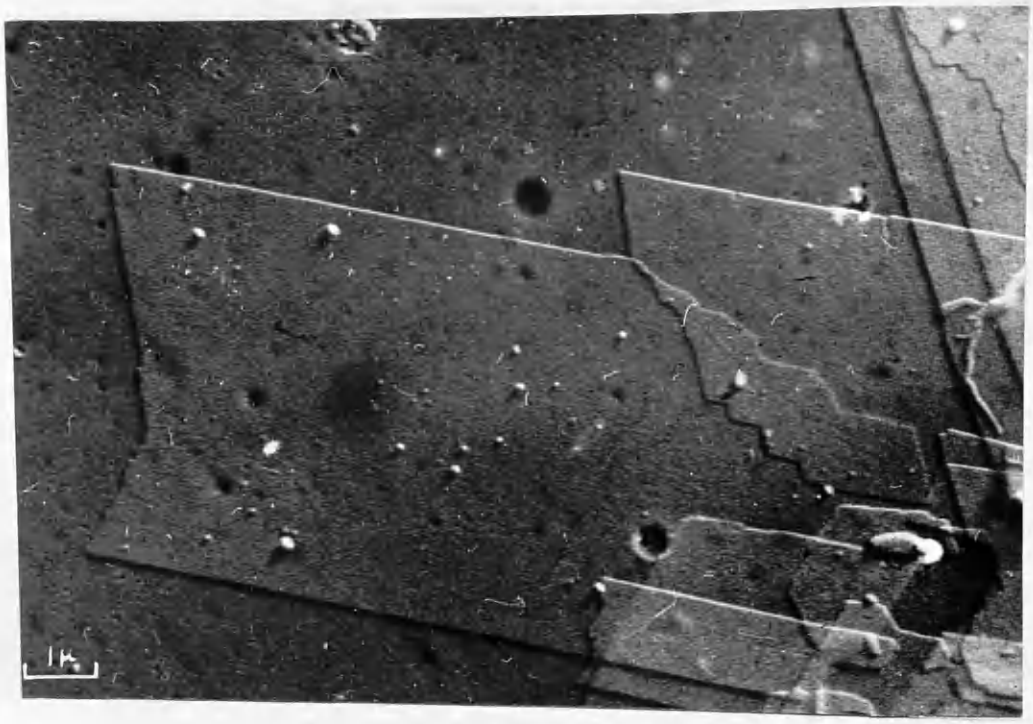

Plate VI

This plate shows a bimolecular twin layer of pentacontanol grown from petroleum ether.

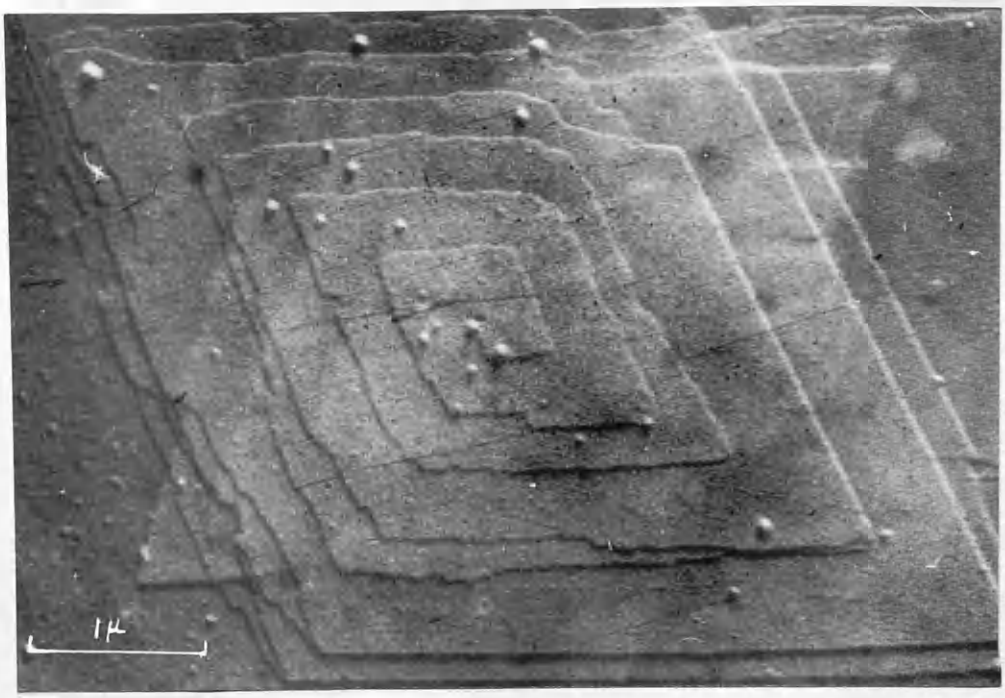

Plate VII

This pentacontanol crystal was grown from petroleum ether and exhibits coalition of monomolecular steps at the crystal edge.

monomolecular ones. It is noteworthy that steps which are close together or which associate in one direction are often far apart in another. It can be seen from Plate VII that step association has occurred on all the edges of the crystal save that at the top of the micrograph.

The twin layers invariably have a thickness corresponding to a bimolecular layer at the growth edge (129 ± 12A° - mean of 44 measurements made on 17 crystals).

The case shown on crystal D in Plate V (page 86) occurs rather infrequently. Only one other of the 31 crystals studied showed two or more monomolecular spirals of the same sense originating from the same point.

The phenomenon of "punch-through" (Anderson and Dawson 1953) was again encountered. On some crystals (e.g. crystal A on Plate V) association appears to have taken place between the original and the punched through steps.

Crystallisation from xylene.

The crystallisation from xylene is more regular than from petroleum ether, as would be expected in view of its lower rate of evaporation. (See Table V, at the end of this section, in which are tabulated the vapour pressures of the solvents used. Strictly speaking the rate of evaporation is not solely determined by vapour pressure. Since heat must be supplied for evaporation to occur, the values of the latent heat and thus also of

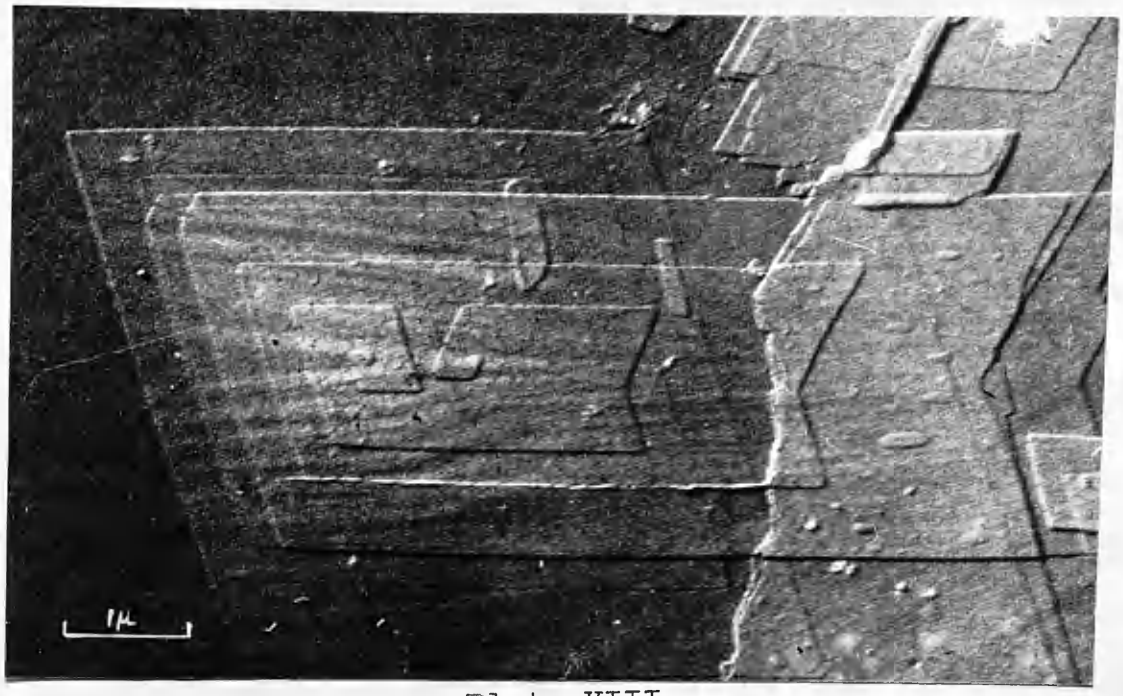

Plate VIII

This pentacontanol crystal was grown from xylene and possesses two bimolecular spirals. Twinned growth has occurred on the right hand half of the crystal.

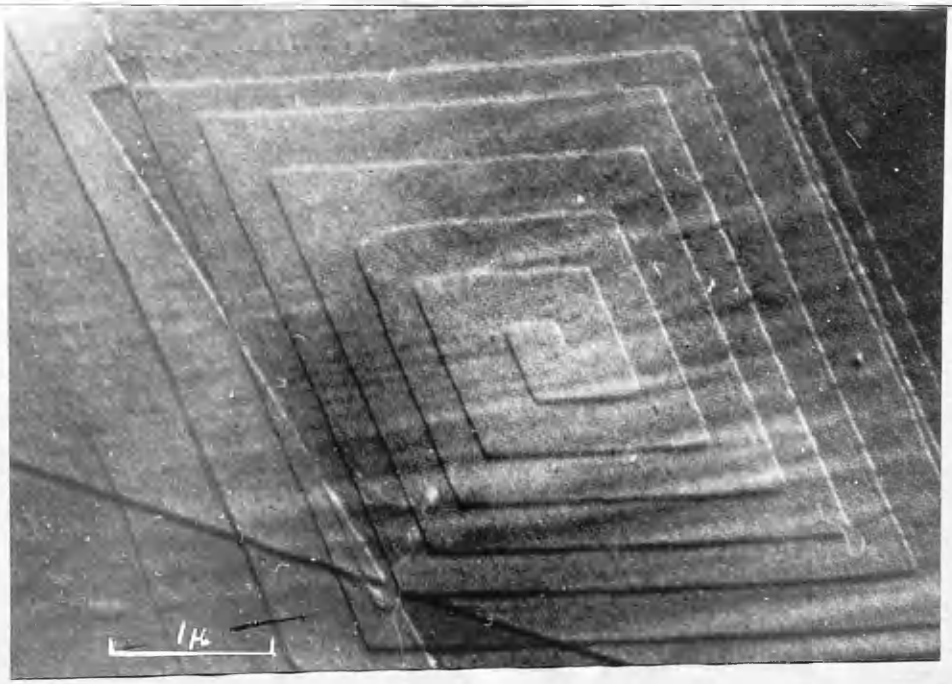

Plate IX

This plate shows a pentacontanol crystal grown from xylene exhibiting monomolecular growth steps.

specific heat and thermal conductivity will also affect the rate of evaporation. However, since we are only concerned here with the evaporation of a small drop of solution, the heat transfer involved will be very small and it is concluded that an approximate measure of relative evaporation rates may be obtained from vapour pressure data.)

Plates VIII, IX (page 90) show fairly regular crystals obtained from xylene solution, although some irregular material is again produced. Twinned laths are again very common (Plate VIII), many of the spiral growth terraces forming part of a twin lath.

The twin layers are once again invariably bimolecular in thickness, ($127 \pm 6A^{\circ}$ - mean of 105 measurements made on 46 crystals). Plate VIII shows a rare case in which only one half of a crystal has become twinned. It is of interest to note that the spiral centres appear to be aligned on the twin boundary of the crystal. Both the spiral and the twin growth steps are bimolecular in this case.

The heights of the other spiral growth steps appear to be approximately equally divided between the monomolecular and the bimolecular types. The step heights of the two groups are $71 \pm 6A^{\circ}$ (mean of 91 measurements made on 25 crystals) and $127 \pm 7A^{\circ}$ (mean of 51 measurements made on 17 crystals). The crystals shown in

Plates IX (page 90) and X (page 93) both possess monomolecular steps. It is interesting to note that the crystal in Plate IX, which possesses monomolecular growth steps, is partly covered by a bimolecular twin layer.

Cancellation of dislocations by punch-through is again observed. The crystal shown in Plate X shows punch-through at a twist boundary in a crystal. Such twist boundaries were found in a variety of long chain compounds including alcohols by Wilman (1951). Anderson and Dawson (1955) observed them on crystals of n-propyl pentacontanoate. These crystals also showed spiral terraces on the upper and lower surfaces which were rotated with respect to each other and which were frequently punched through. The twist on the crystal shown in Plate X is 67°, which corresponds to the crystallographic angle and also to the inclination between the two portions of a twinned lattice.

Crystallisation from carbon tetrachloride.

The crystallisation from this solvent was found to be irregular in the extreme and it was difficult to determine whether the observed growth steps were due to spiral growth or not. Accordingly no step heights were measured in this case. Several unsuccessful attempts were made to achieve more regular crystals and it was concluded that no better crystals could be obtained from this solvent whose rate of evaporation is appreciably

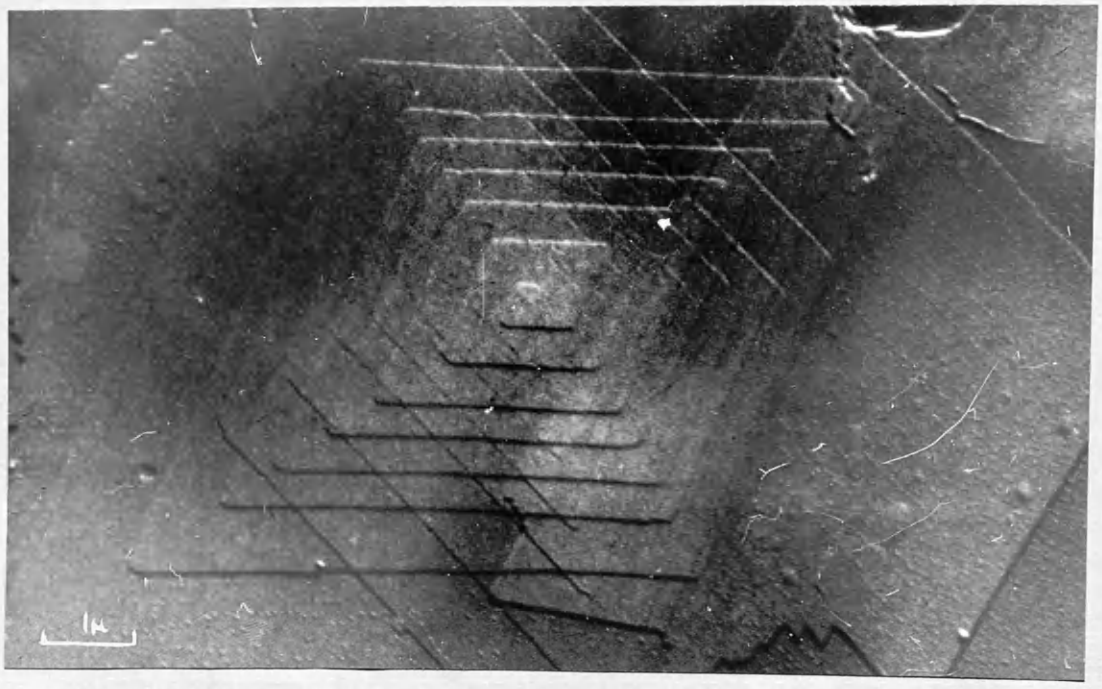

Plate X

This pentacontanol crystal grown from xylene exhibits punch through at a twist boundary. The upper and lower surfaces of the crystal are oriented at 67° to each other. The steps are monomolecular.

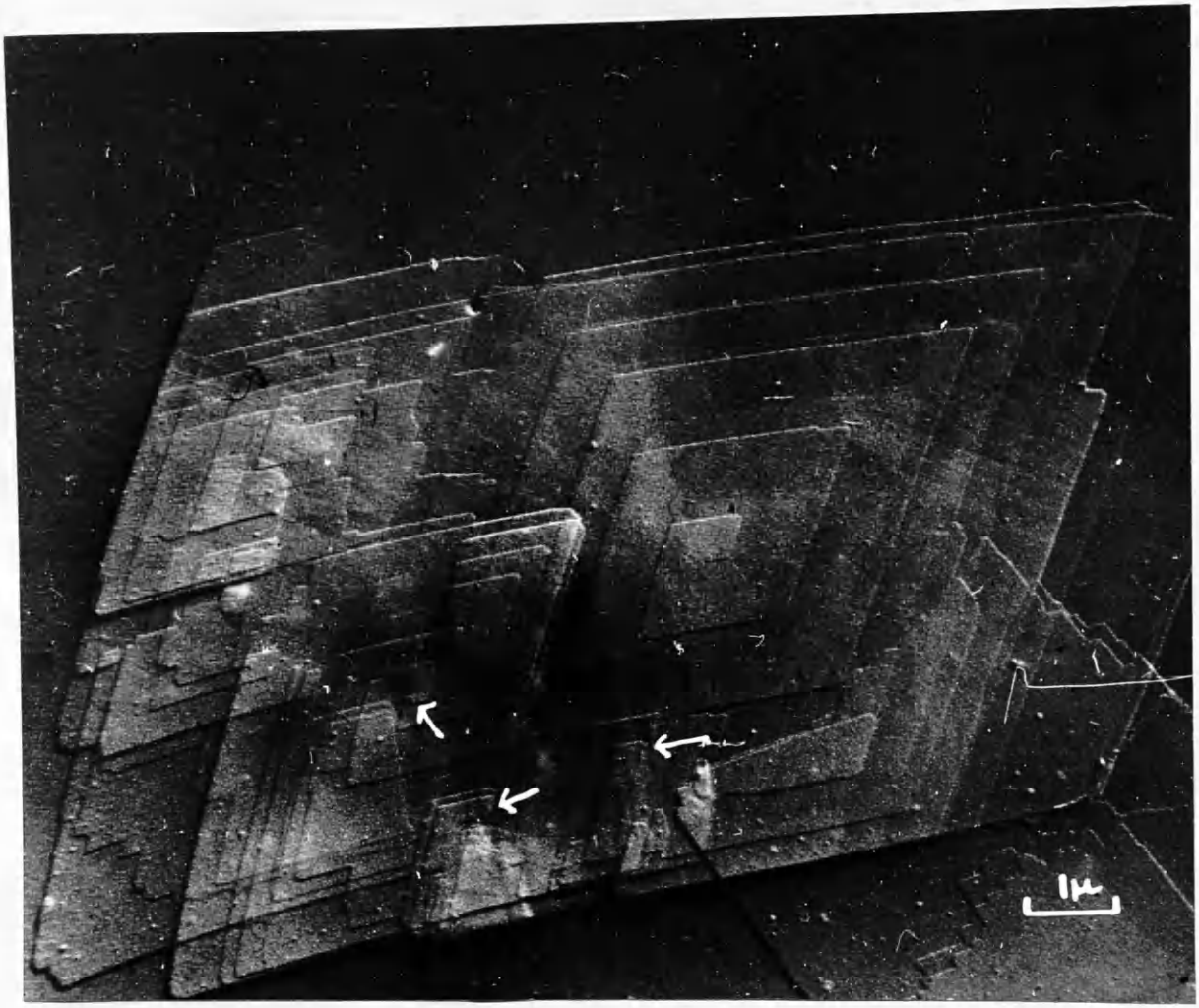

Plate XI

This pentacontanol crystal grown from amyl acetate shows several monomolecular growth spirals. The arrows indicate sites at which there are two or more spirals of the same sense originating at the same point.

greater than that of petroleum ether (see Table V).

Crystallisation from amyl acetate.

When amyl acetate was used as a solvent extremely regular crystals were obtained. These were in general comparitively large discrete crystals. Very few twin layers were observed. Most of the crystals possess monomolecular growth steps (Plate XI, page 94, Plate XII, page 96 ; step heights 70 ± 5A° - mean of 157 measurements made on 51 crystals). However two of the 53 crystals studied did show bimolecular steps (heights 127A°, 132A° - mean of 2 measurements in each case). One of these crystals is shown in Plate XIII* (page 96). This contrasts sharply with the xylene crystallisation in which 17 crystals out of 42 showed bimolecular spirals.

In the few cases in which twin layers are found among this batch of crystals they are again invariably bimolecular (step height 130 ± 6A° - mean of 14 measurements made on 5 crystals). Such a twin is shown in Plate XIV (page 97).

The large crystal in Plate XI shows several instances of two monomolecular spirals of the same sense originating at the same point. It is important

*It should be noted that punch through has occurred on the crystal in Plate XIII. However in measurement of step height, care was taken to avoid complex steps produced by punch-through.

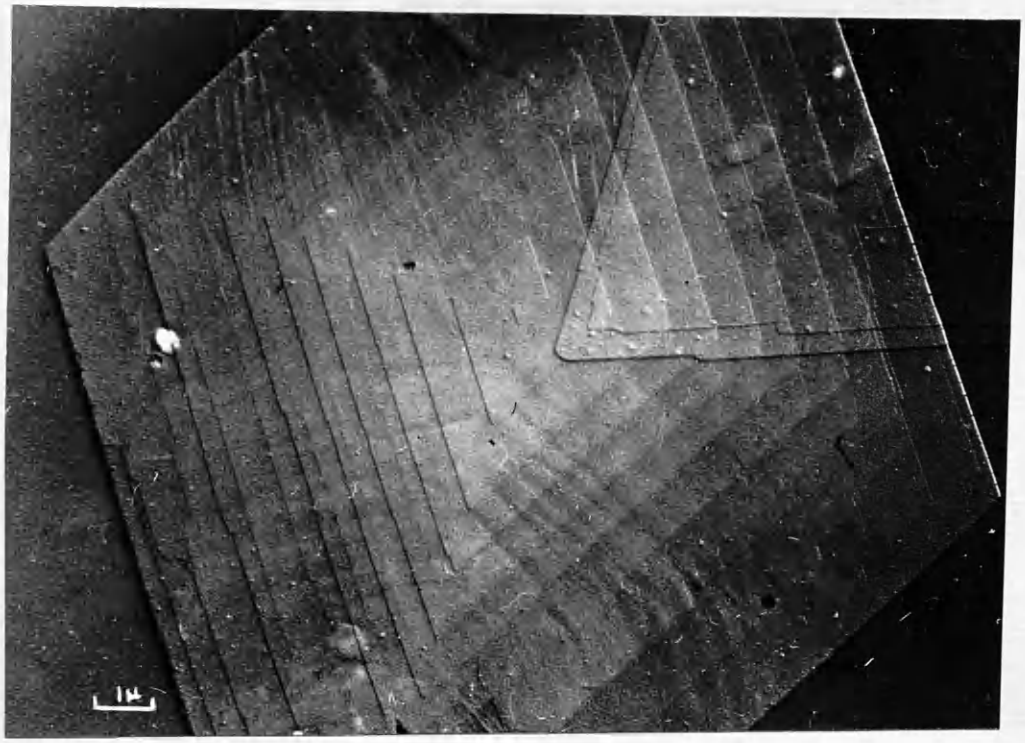

Plate XII

This micrograph shows a pentacontanol crystal grown from amyl acetate possessing monomolecular growth steps.

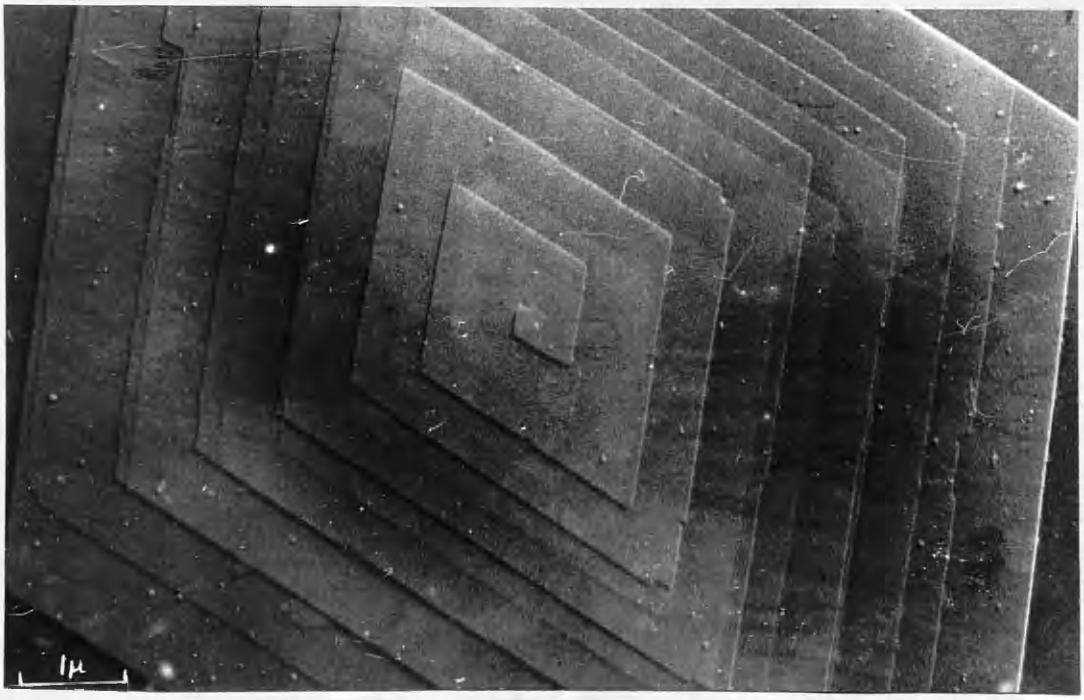

Plate XIII

This plate shows one of the two crystals of pentacontanol grown from amyl acetate which exhibits bimolecular growth steps.

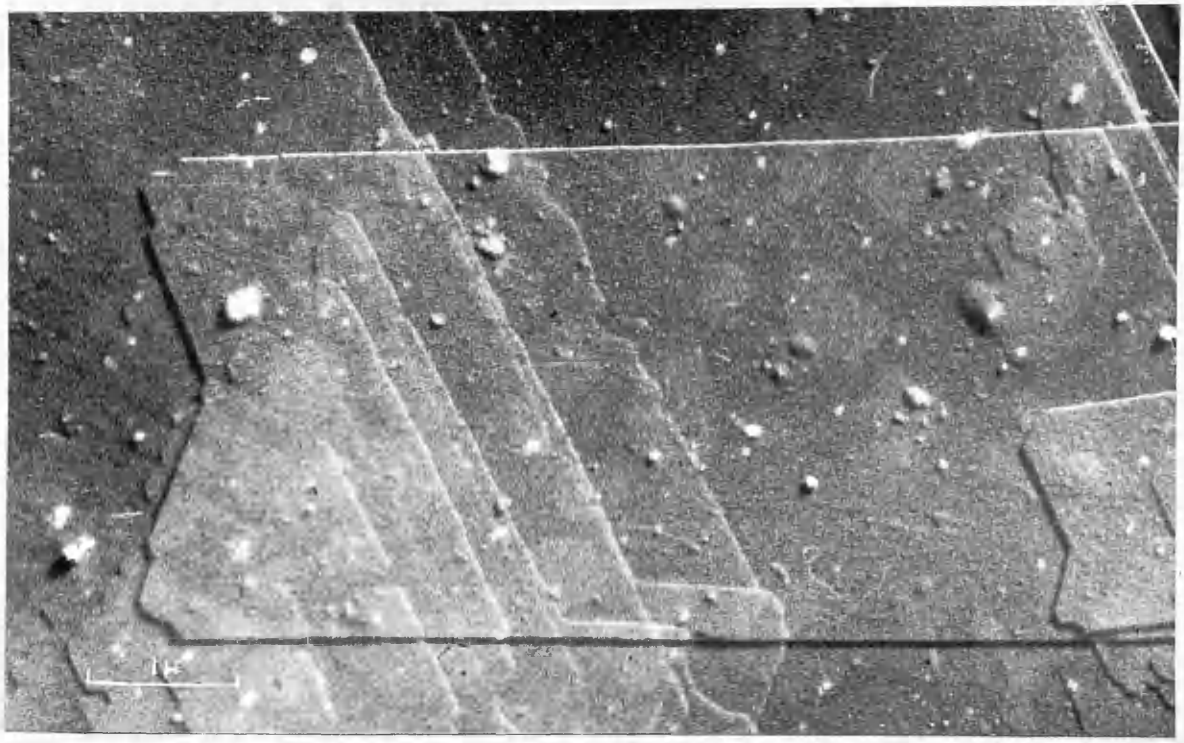

Plate XIV

This micrograph shows a bimolecular twin layer of pentacontanol grown from amyl acetate solution.

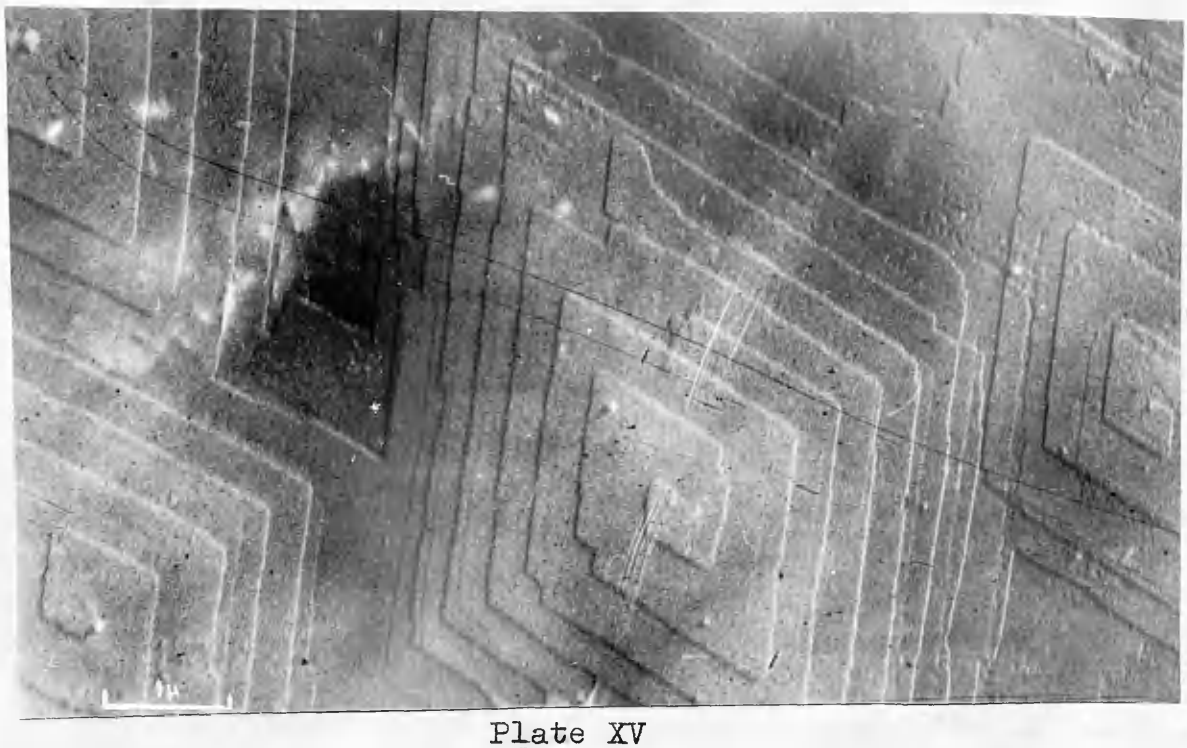

Plate XV

This micrograph shows the sheet like growth of pentacontanol from dioxan. All the steps are monomolecular.

to note that such intertwined spirals exist on 16 of the 53 crystals grown from amyl acetate solutions. On the other hand none of the 42 crystals grown from xylene solutions exhibit this phenomenon (see Table III at the end of this section).

Many of the crystals possess punched through spirals. However none of the crystals with two intertwined spirals exhibit punch through.

Crystallisation from dioxan.

Amyl acetate evaporated rather more slowly than xylene but dioxan provides an example of a polar solvent whose rate of evaporation is greater than that of xylene (Table V),

All the crystals studied exhibited monomolecular steps (height 69 ± 6A^{o} - mean of 81 measurements made on 31 crystals). Growth is generally fairly regular, although very often large sheet like crystals are formed with many spiral terraces (Plate XV, page 97). Crystals of this type are also obtained from amyl acetate solutions occasionally (e.g. Plate XI, page 94).

Crystallisation from iso-propyl alcohol.

Iso-propyl alcohol evaporates more readily than xylene (Table V). When however it is used as a solvent for the crystallisation of n-pentacontanol, the crystallisation, although less regular than from amyl acetate,

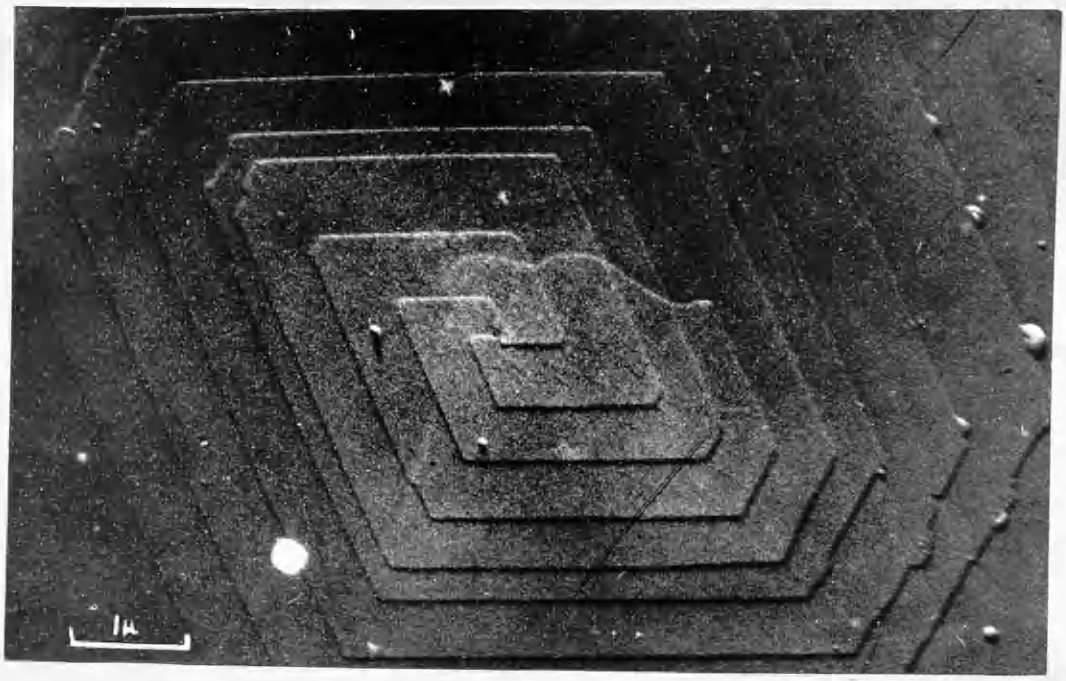

Plate XVI

This pentacontanol crystal grown from iso-propyl alcohol possesses three co-operating bimolecular spirals of the same sense. The development of additional edges in the growth from this solvent is also illustrated.

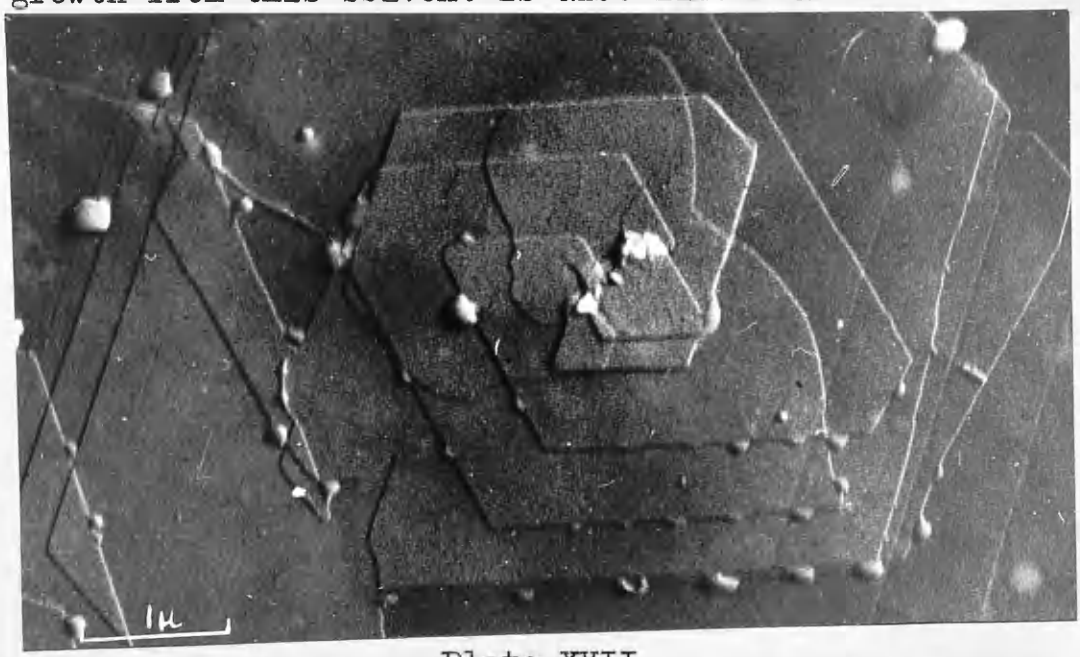

Plate XVII

This pentacontanol crystal grown from iso-propyl alcohol also exhibits the additional edges. Two of the three bimolecular spirals are oriented at 67° to the third. The twist boundary is thus between spirals of the same sense.

is more regular than from xylene.

An additional feature of the growth from this solvent is the presence of two extra edges on the crystals (Plates XVI, XVII - page 99). These additional faces do not disappear towards the edge of the crystal. In fact, like the normal faces, they increase in length towards the periphery.

In Plate XVII is shown a crystal with three bimolecular spirals of the same sense, one of which is oriented at 67° to the other two. This case has not previously been observed in the electron microscopy of long chain compounds. It is, however, somewhat similar to the case studied by Amelinckx (1953b,c,1954) in which two interlaced spirals are oriented at 60° to each other.

Both mono- and bi-molecular steps are found on the crystals grown from this solvent (heights 72 ± 8A° - mean of 52 measurements made on 20 crystals and 126 ± 6A°- mean of 72 measurements made on 25 crystals).

When crystals were grown from aqueous iso-propyl alcohol, the result is as shown in Plate XVIII (page 101). This crystal was grown from a solution to which an appreciable amount of water has been added. It is seen that the additional face effect is accentuated, the two extra faces now being equal in length to the normal faces, so that an almost hexagonal crystal results. The surface of the crystal also appears to be cracked in certain

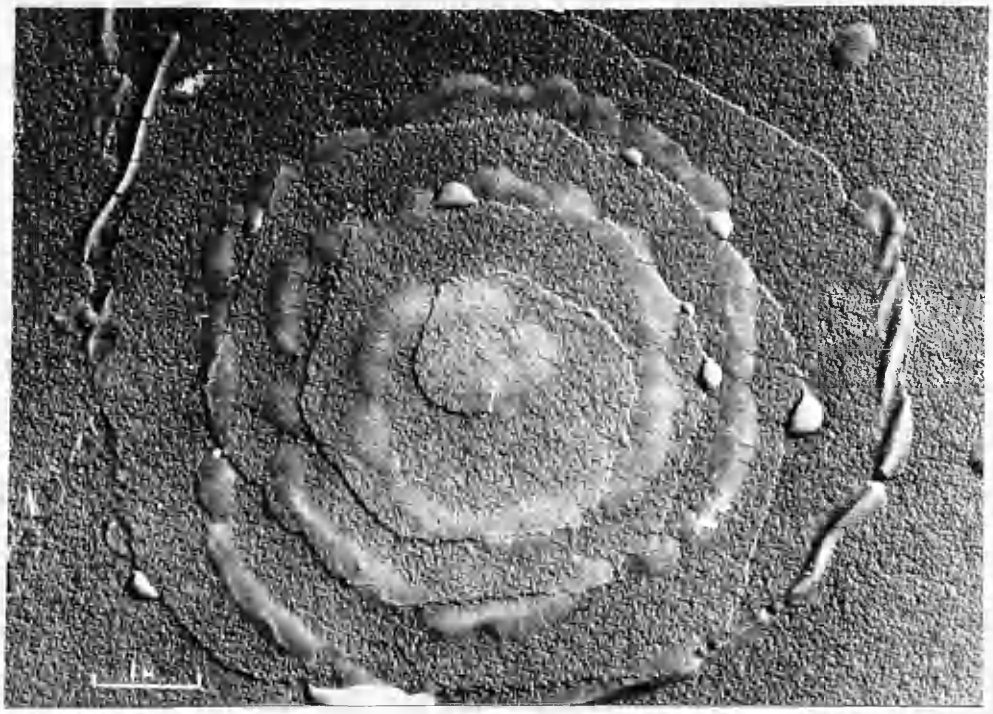

Plate XVIII

This pentacontanol crystal was grown from a very aqueous solution in iso-propyl alcohol and shows the exaggeration of the additional face effect under these conditions.

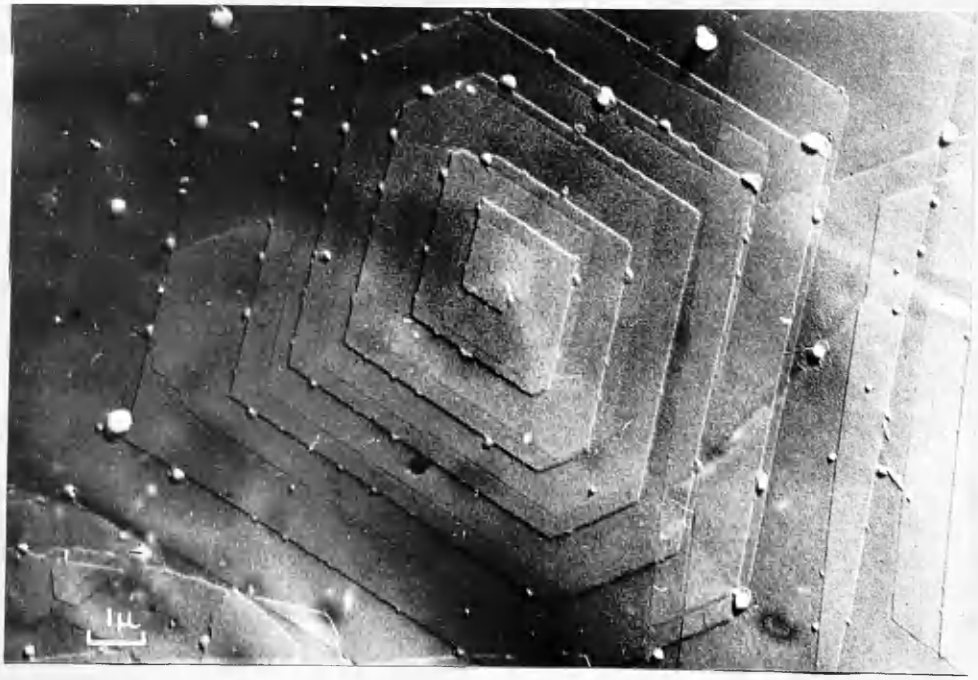

Plate XIX

This plate shows a pentacontanol crystal grown from iso-propyl alcohol possessing regular additional faces.

places.

In the examples so far described, the additional faces are rather irregular. However Plate XIX shows that the additional faces can be just as regular as the normal faces.

An outstanding feature of this crystallisation is the complete absence of twinned crystals.

Crystallisation from n-propyl alcohol.

The growth from n-propyl alcohol resulted in crystals similar to those obtained from iso-propyl alcohol solutions.

However most of the crystals grown from solutions in dried n-propyl alcohol were of the normal shape (Plate XX, page 103). It will be seen that this crystal possesses two spirals which are oriented at 8°. The two spirals in this case are monomolecular. This case has been excluded from the analysis in Table III, since it appears to differ slightly from the normal case of a dissociated bimolecular dislocation.

Monomolecular and bimolecular steps occur on both types of crystal grown from this solvent (step heights $72 \pm 6A^{\circ}$ - mean of 103 measurements made on 41 crystals and $128 \pm 6A^{\circ}$ - mean of 62 measurements made on 24 crystals).

As in the previous crystallisation no twins were observed.

Plate XX

This pentacontanol crystal was grown from dried n-propyl alcohol and does not possess the additional faces. The two monomolecular spirals are oriented at an angle of 8° to each other.

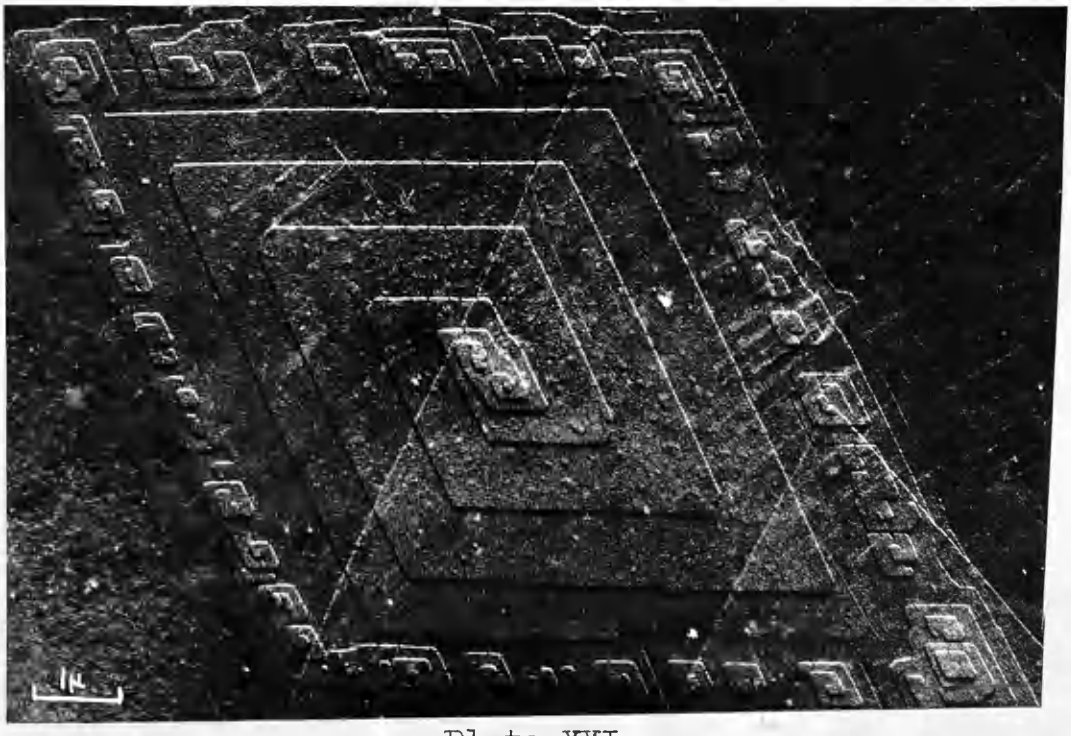

Plate XXI

This pentacontanol crystal grown from n-butyl alcohol is of the normal form and illustrates the formation of screw dislocations at the crystal edge.

Crystallisation from n-butyl alcohol

N-butyl alcohol as normally obtained contains very little moisture. Correspondingly, crystals grown from this solvent were found to be of the normal form (Plates XXI , XXII - pages 103 and 105.) . When water was added to the solution however, the additional faces were again observed (Plates XXIII, XXIV, XXV - pages 105 and 106). The crystals shown in these three plates were grown from solutions made successively more aqueous. It is seen that as the water content of the solution is increased, so the additional edges become greater in length. These results are consistent with the result obtained when crystals were grown from a solution in iso-propyl alcohol to which an appreciable amount of water had been added (Plate XVIII, page 101).

The crystals shown on Plate XXIII were grown from a solution which was only very slightly aqueous. The additional faces are not very pronounced and are only shown by the outermost (i.e. first formed) layers of the spiral terrace.

In Plate XXI (page 103) is shown a crystal with a spiral originating at the centre, which possesses many small spirals round the edge. This phenomenon has also been observed on a crystal of n-hectane (Anderson and Dawson 1955).

Both mono- and bi-molecular steps were again observed on this batch of crystals (step heights

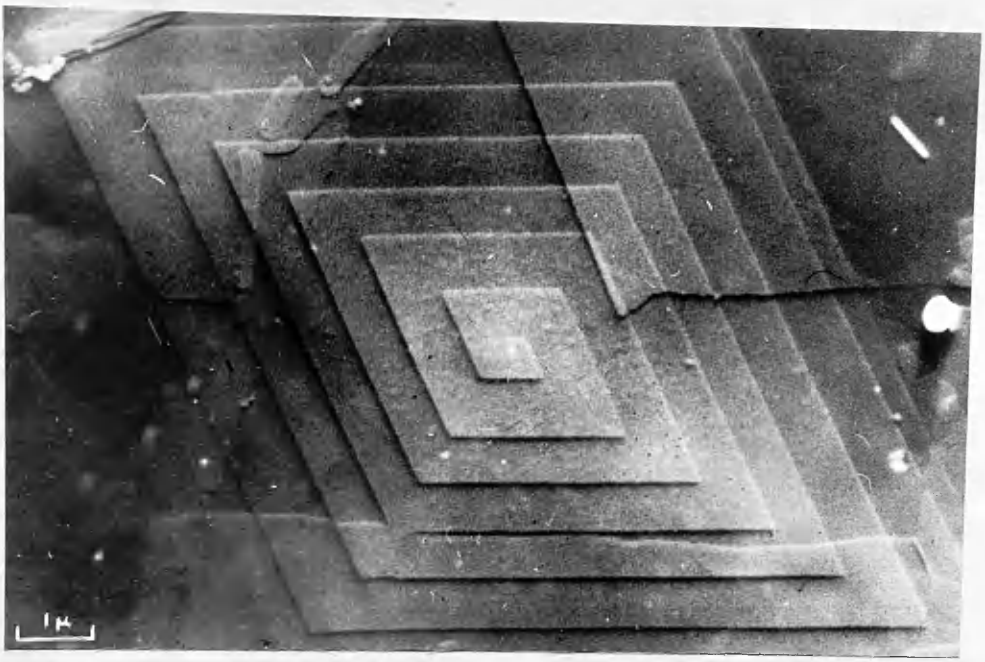

Plate XXII

This micrograph shows a crystal of pentacontanol grown from n-butyl alcohol, which is of the normal form.

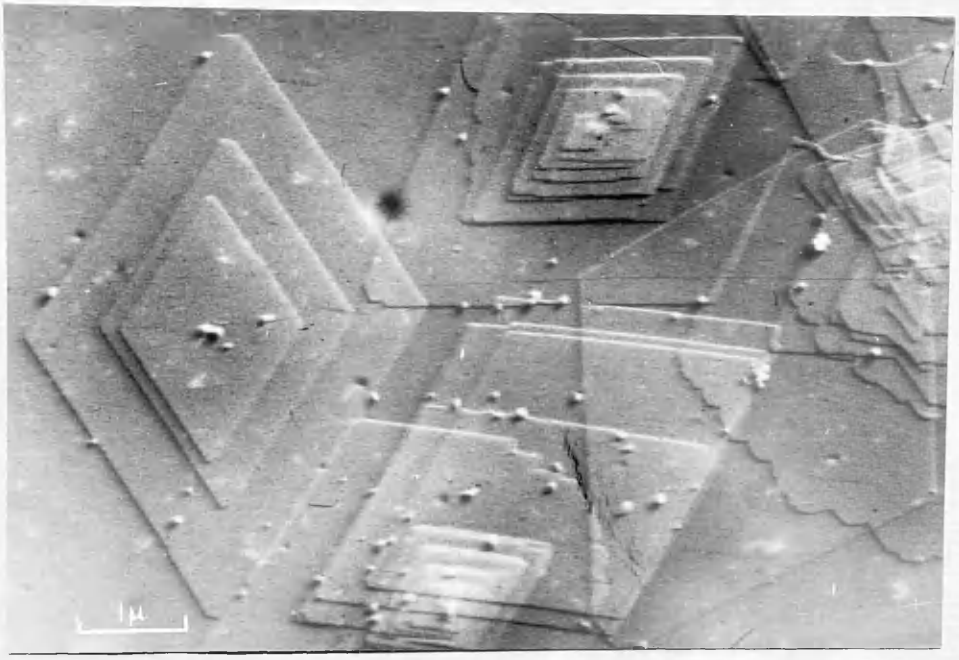

Plate XXIII

These pentacontanol crystals were grown from very slightly aqueous n-butyl alcohol. The additional edges are not very pronounced.

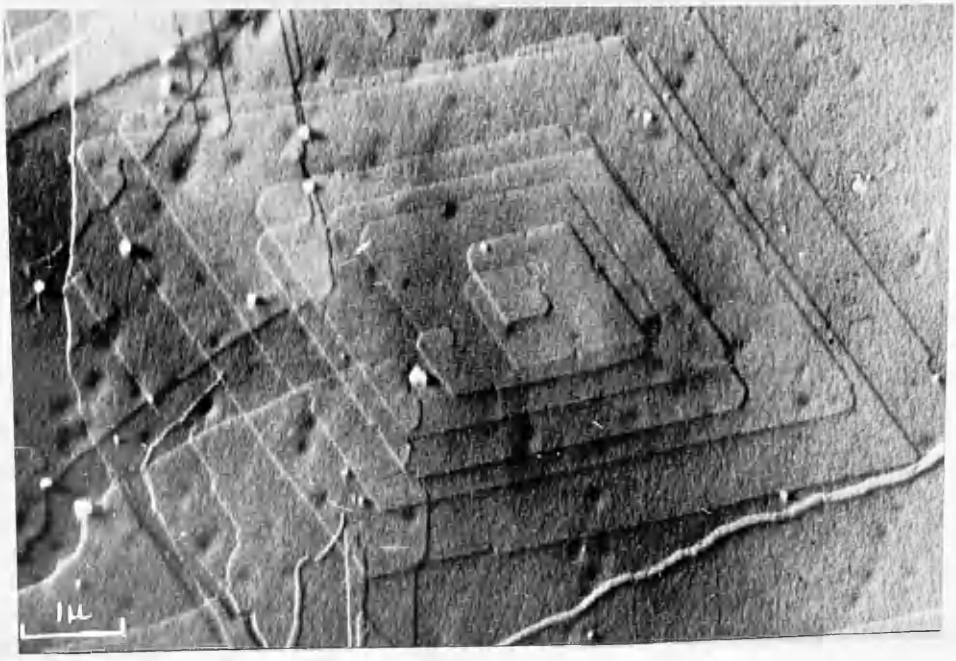

Plate XXIV

This micrograph shows pentacontanol crystals grown from a slightly more aqueous solution in n-butyl alcohol. The additional edges are more pronounced.

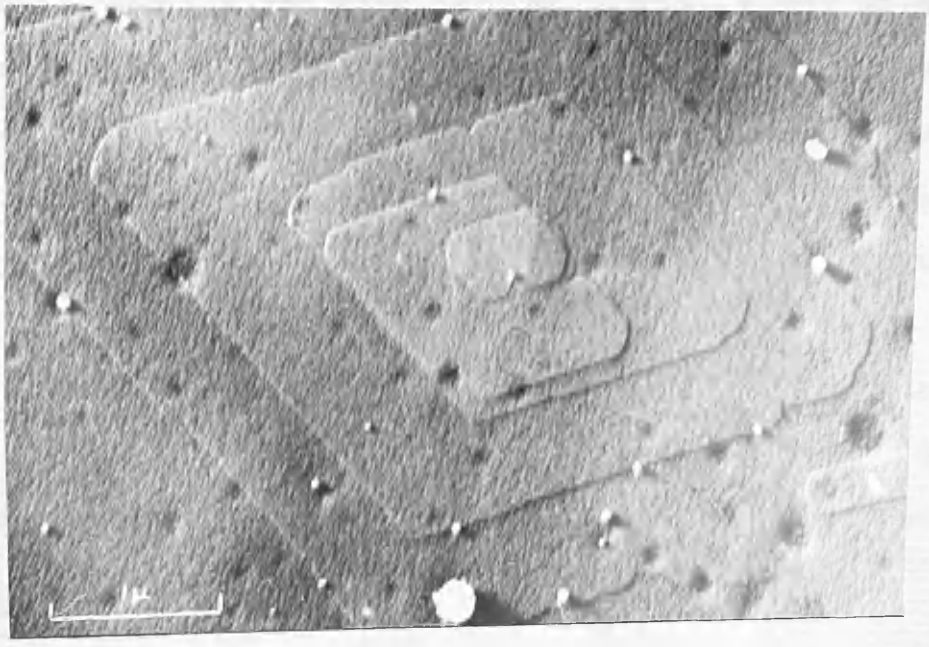

Plate XXV

These pentacontanol crystals were grown from an even more aqueous solution in n-butyl alcohol. The additional edges are now quite marked.

73 ± 6A° - mean of 121 measurements made on 34 crystals and 128 ± 7A° - mean of 58 measurements made on 16 crystals).

Once again no twinned crystals were observed.

Crystallisation from n-amyl alcohol.

The crystallisation from this solvent is similar to that from amyl acetate. The crystals are of the normal type, although once again the additional faces are observed on crystals grown from aqueous solutions.

There is one outstanding difference in the growth from this solvent as compared with the other alcohol solvents. All the steps measured are monomolecular (step height 67 ± 5A° mean of 125 measurements made on 54 crystals). Further this solvent, alone of all the alcohols, gives crystals showing two monomolecular spirals of the same sense and point of origin. In this it again resembles amyl acetate.

However it does show one common feature with the other alcohol solvents in that no twins were observed among the crystals obtained in this batch.

The crystal in Plate XXVI (page 108) exhibits punch-through. As on crystal A of Plate V (page 86) association appears to have occurred between the original and punched through steps.

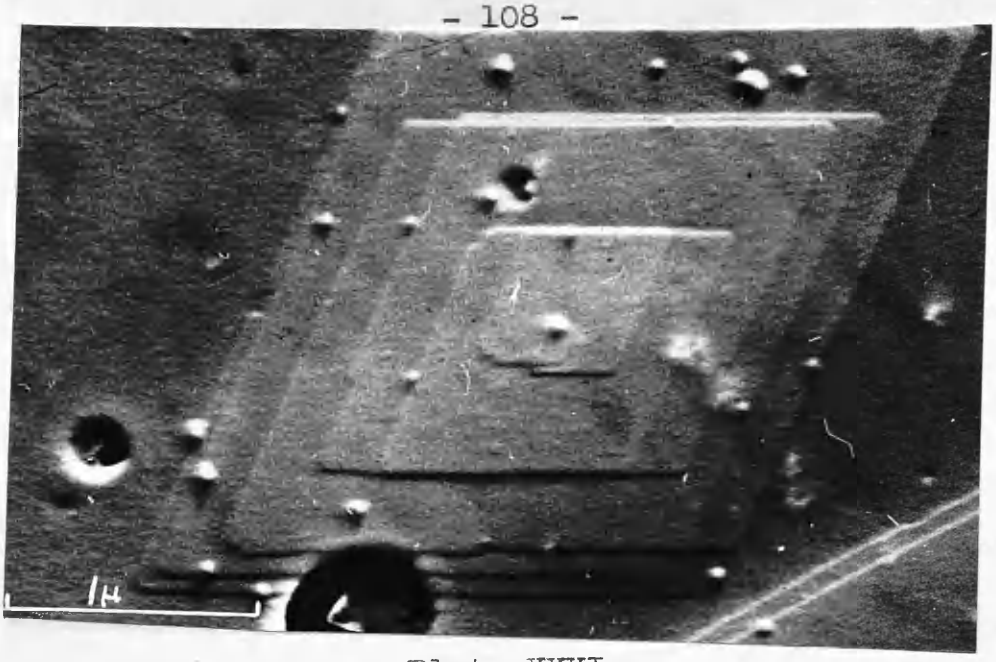

Plate XXVI

This pentacontanol crystal grown from amyl alcohol exhibits coalition of the monomolecular steps of the spirals on the upper and lower surfaces after punch-through.

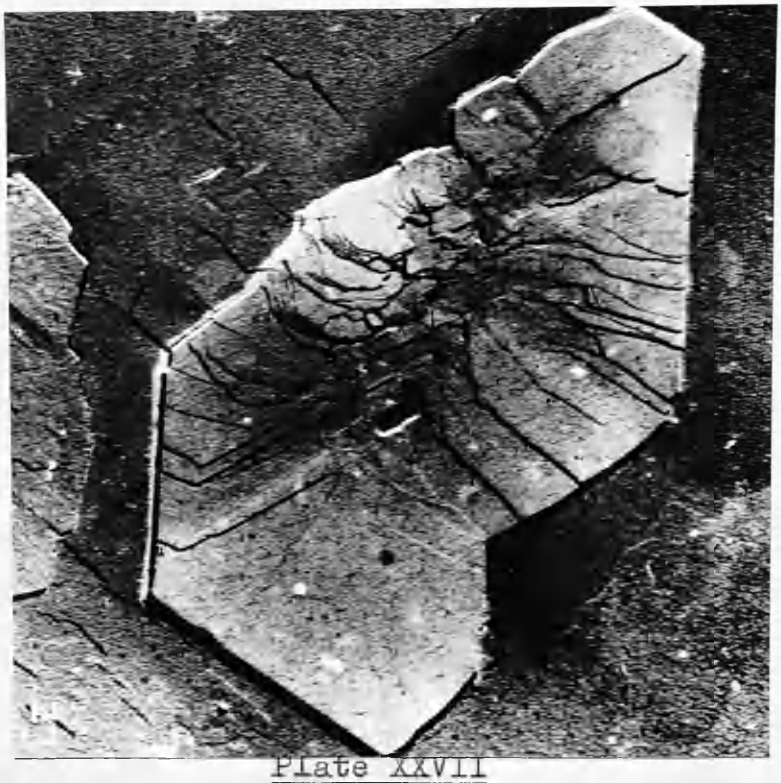

Plate XXVII

This plate shows a pseudo-replica of a pentacontanol crystal grown from xylene at 90° (unrestricted evaporation). Multimolecular steps occur and the crystal is hexagonally shaped.

High temperature crystallisations from xylene.

Crystallisation at 90° (unrestricted evaporation).

The crystallisation at about 90° with unrestricted evaporation gave crystals which did not give clear evidence of the presence of spiral growth steps (Plate XXVII, page 108 and Plate XXVIII, page 110). Multimolecular steps of varying height do occur, however, on the surface of the crystals. The heights were found to correspond to steps of two to six molecules high. Large steps appear to have been formed in some instances from the coalition of smaller ones.

A large number of the crystals were hexagonal in shape (plate XXVII) although some crystals of the normal form were also observed (Plate XXVIII).

In contrast to the crystallisation from xylene at room temperature, no twinned crystals were observed in this case.

Crystallisation at 40° (controlled evaporation).

The crystals obtained in this instance exhibited spiral growth terraces. The spirals are still rectilinear in shape, but are slightly more irregular than those observed at room temperature (Plate XXIX, page 110). Most of the crystals possess monomolecular steps (height 66 ± 5A° mean of 61 measurements made on 23 crystals) but there were also some with bimolecular steps (height 127 ± 6A°

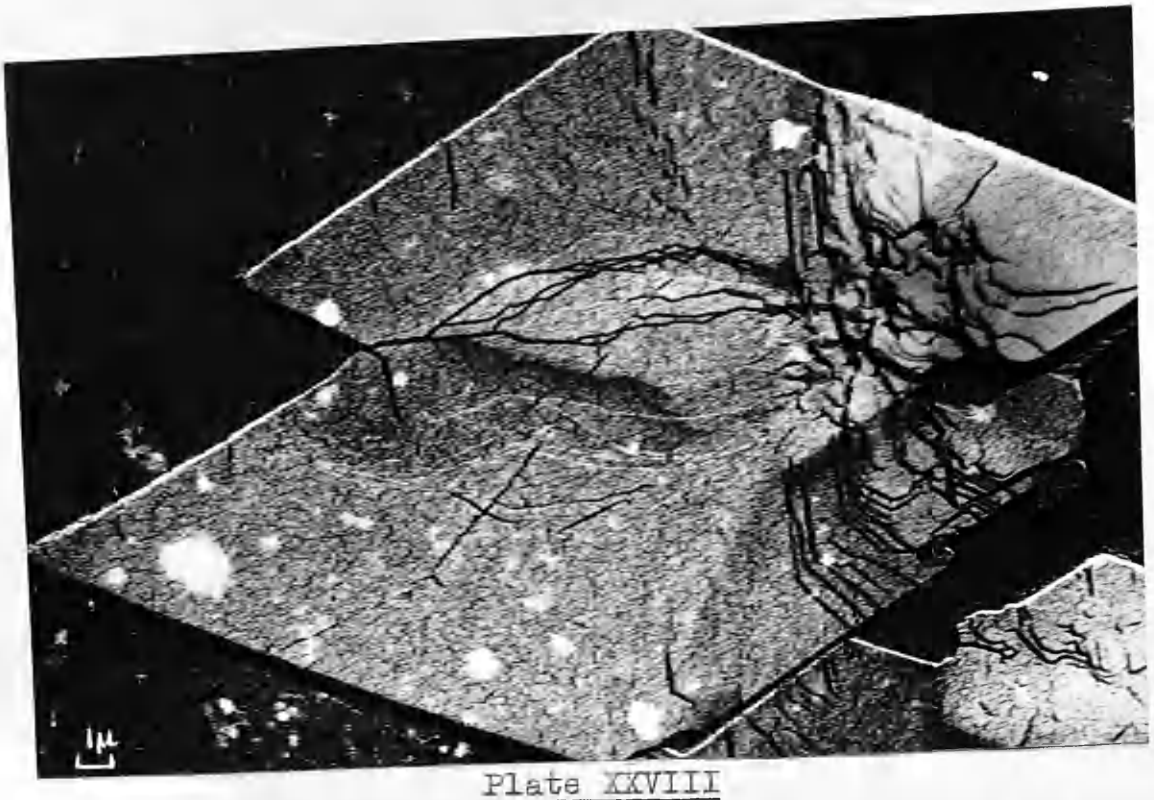

Plate XXVIII

This plate shows a pseudo-replica of another pentacontanol crystal grown at 90° (unrestricted evaporation). This crystal is of the normal form, although once again no spirals are visible.

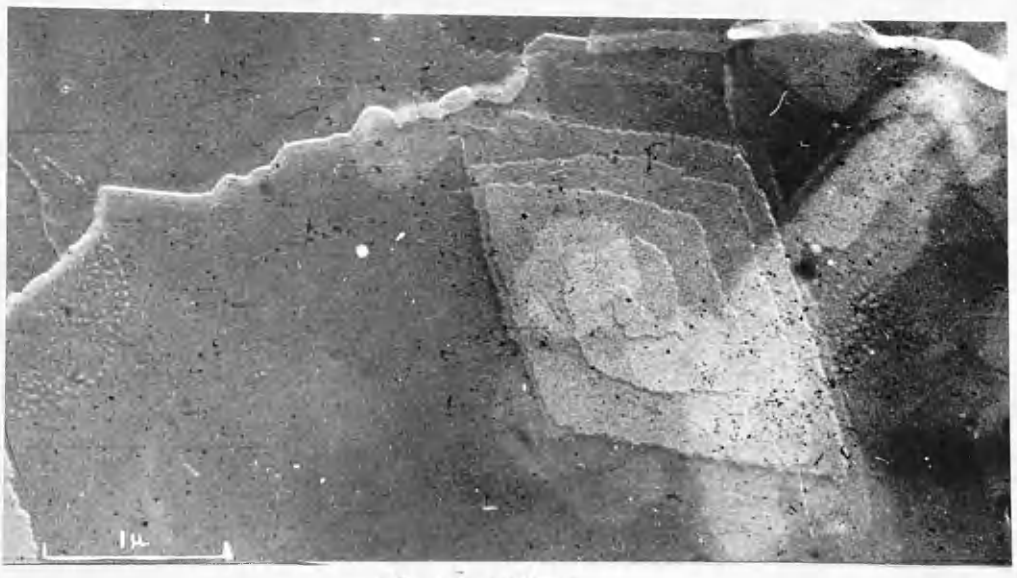

Plate XXIX

This pentacontanol crystal was grown from xylene at 40° (controlled evaporation) and shows one of the slightly irregular spirals which result.

mean of 12 measurements made on 3 crystals). (The step height measurements for the high temperature crystallisations are summarised in Table IV). Several twin crystals were observed.

Crystallisation at 50° (controlled evaporation).

The crystals obtained at 50° still showed spiral growth but the spirals are now much more irregular, tending towards a circular shape (Plate XXX, page 112). There is also evidence of a tendency towards island nucleation at certain points.

Monomolecular steps were observed on all but one of the crystals studied (height 69 ± 7A° - mean of 63 measurements made on 27 crystals). The only crystal showing bimolecular steps (height 133A° - mean of 2 measurements) was also the only twin crystal observed in this crystallisation.

Crystallisation at 60° (controlled evaporation).

No evidence of spiral growth was found on the crystals of this batch. The crystals appear to grow by layer growth (Plate XXXI, page 112). All these layers were found to be monomolecular, although on some crystals bimolecular layers are formed by coalition of monomolecular ones. No multimolecular layers were observed. There was a tendency for formation of hexagonally shaped crystals in some instances. No twinned crystals were observed.

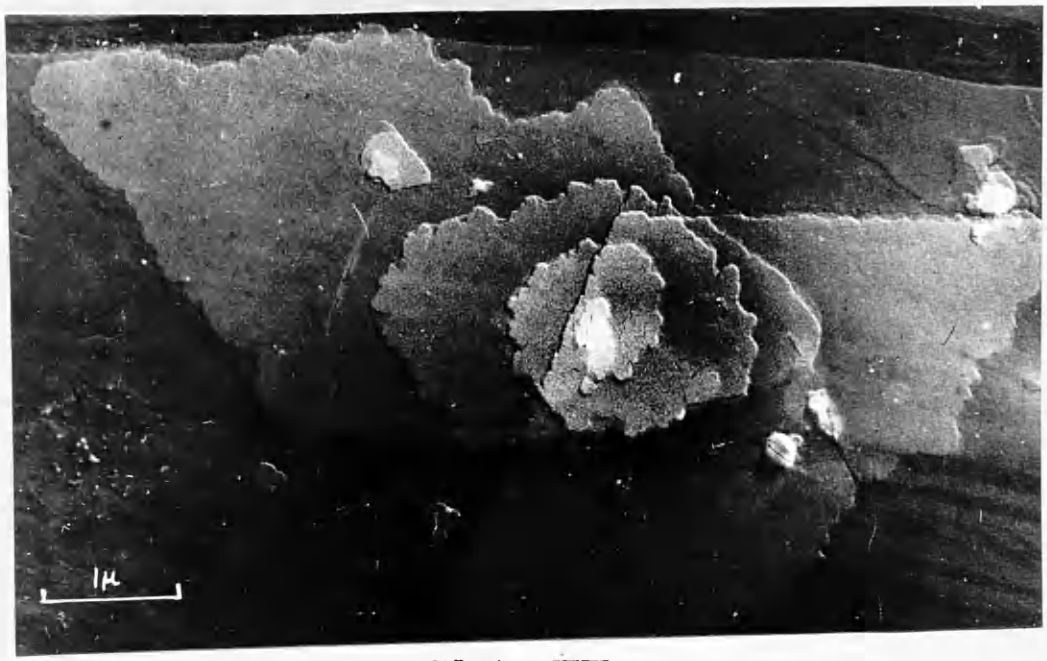

Plate XXX

This pentacontanol crystal was grown from xylene at 50° - the spiral has become much more irregular in outline.

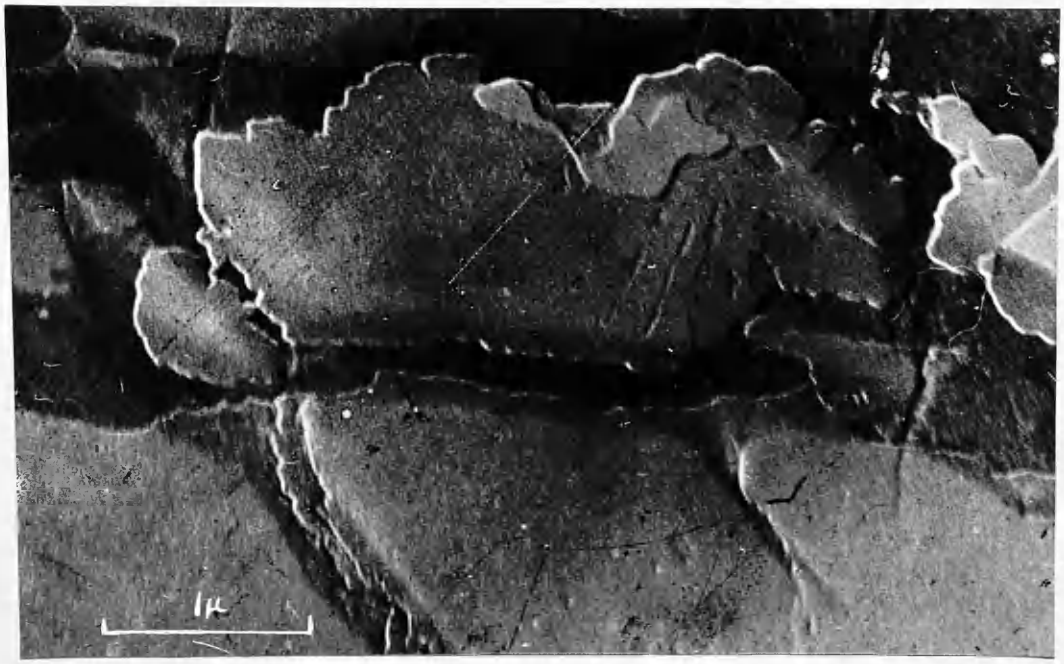

Plate XXXI

This plate shows the irregular layer growth resulting from xylene at 60°. No spirals are visible but no multimolecular spirals occur provided that the evaporation is restricted.

Crystallisation at 90° (controlled evaporation).

Most of the crystals in this batch were hexagonal in form but otherwise this crystallisation exhibits the same characteristics as the last one. No multimolecular steps were observed, this result contrasting sharply with that obtained in the crystallisation at about 90° with uncontrolled evaporation.

TABLE II

SUMMARY OF STEP HEIGHT MEASUREMENTS.

Group	Solvent	Type of step	Step height	No. of measure-ments	No. of crystals studied
NON-POLAR	Pet. ether	Spiral (1-mol)	69 ± 7A°	60	24
		Spiral (2-mol)	133 ± 7A°	16	7
		Twin	129 ± 12A°	44	17
	Xylene	Spiral (1-mol)	71 ± 6A°	91	25
		Spiral (2-mol)	127 ± 7A°	51	17
		Twin	127 ± 6A°	105	46
POLAR	Amyl acetate	Spiral (1-mol)	70 ± 5A°	157	51
		Spiral (2-mol)	127, 132A°	4	2
		Twin	130 ± 6A°	14	5
	Dioxan	Spiral (1-mol)	69 ± 6A°	81	31
ALCOHOLS	Iso-propyl alcohol	Spiral (1-mol)	72 ± 8A°	52	20
		Spiral (2-mol)	126 ± 6A°	72	25
	N-propyl alcohol	Spiral (1-mol)	72 ± 6A°	103	41
		Spiral (2-mol)	128 ± 6A°	62	24
	N-butyl alcohol	Spiral (1-mol)	73 ± 6A°	121	34
		Spiral (2-mol)	128 ± 7A°	58	16
	N-amyl alcohol	Spiral (1-mol)	67 ± 5A°	125	54

TABLE III

DETAILED ANALYSIS OF STEP HEIGHT RESULTS.

	Solvent	No. crys.	Monomolecular steps			Bimolecular steps			% Mono	% Bi
			Single spiral	2 spirals		Single spiral	2 spirals			
				Same sense	Opposite sense		Same sense	Opposite sense		
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
NON POLAR	Pet. ether	31	20	2	2	6	0	1	77	23
	Xylene	42	22	0	3	13	0	4	60	40
POLAR	Amyl acetate	53	28	16	7	1	1	0	96	4
	Dioxan	31	27	2	2	0	0	0	100	0
ALCOHOLS	Iso propyl	45	18	0	2	20	3*	2	44	56
	N -propyl	65	37	0+	4	23	1	0	63	37
	N-butyl	50	32	0	2	16	0	0	68	32
	N-amyl	54	49	3	2	0	0	0	100	0

*Includes the cases shown in Plates XVI, XVII in which there are three co-operating spirals of the same sense.

+Does not include case of Plate XX in which two monomolecular spirals are at different orientations (see page 102)

TABLE IV

EFFECT OF TEMPERATURE ON STEP HEIGHT.

(a) Summary of measurements.

Temp.	No. of crys. studied	No. of measurements made	Step height
Room temp.	25	91	71 ± 6A°
	17	51	127 ± 7A°
40°	23	61	66 ± 5A°
	3	12	127 ± 6A°
50°	27	63	69 ± 7A°
	1	2	133A°

(b) Results as percentages.

Temp.	No. of crys. studied	No. of crys. with 1-mol steps	No. of crys. with 2-mol steps	% of crys. with 1-mol steps	% of crys. with 2-mol steps
Room	42	25	17	60%	40%
40°	26	23	3	88%	12%
50°	28	27	1	96%	4%

TABLE V

VAPOUR PRESSURES OF SOLVENTS USED.*

Solvent	V.P. at 20°	Notes
Carbon tetrachloride	91.0 mms.	
Heptane (b.p. 98°)	35.5 mms.	V.P. will approximate to that of pet. ether
Iso-propyl alcohol	32.0 mms.	
Dioxan	27.0 mms.	
N-propyl alcohol	14.5 mms.	
Xylene (ortho)	10.0 mms.	Coal tar xylene is a mixture of all three, meta representing 70-85%
(para)	16.3 mms.	
(meta)	6.4 mms.	
N-butyl alcohol	4.4 mms.	
N-amyl alcohol	2.8 mms.	
Amyl acetate	6.5 mms.	

*The values given were extracted from the International Critical Tables with the exception of those for iso-propyl alcohol and dioxan. No values were given for these in the tables and the values quoted are taken from data compiled by Durrans (1944).

(b) STATISTICAL ANALYSIS OF THE STEP HEIGHT RESULTS.

It was to be expected that, on the basis of step height measurements, the solvents would fall into two groups, namely polar and non-polar. However an examination of the data in Table III (page 115) suggests that there are in fact three groups, since the alcohol solvents seem to show appreciable differences from the polar solvents in the matter of step heights. Since the differences between the three groups may only be due to sampling errors, the results were examined statistically. The test of significance described by Weatherburn (1949) was employed.

Table VI (page 119) shows the results of a test of significance of the difference in proportions of bimolecular steps observed in the growth from non-polar and polar solvents. The non-polar solvent xylene is taken as a standard and the results for the polar solvents are compared with it individually. Table VII (page 120) shows a test of the difference between the polar and alcohol solvents, the polar solvent amyl acetate being used as a standard.

A cursory examination of Table III suggests that there may be a difference in the results for the members of one group of solvents. Accordingly in Tables VIII, IX, X the various groups are tested using one member of the group as a standard. In the case of the alcohols two tests were carried out : one (Table Xa) using iso-propyl

and the second (Table Xb) butyl alcohol as a standard.

Table III shows that there are far more examples of two monomolecular spirals of the same sense on crystals of pentacontanol grown from polar solvents than there are on those grown from non-polar solvents. In Table XI (page 121) therefore, the significance of this difference is tested using xylene as standard. Since we presume these spirals to result from a bimolecular layer, we must take N (and N_o) as the number of bimolecular layers nucleated which have given rise to dislocations. Thus N (or N_o) is the sum of the figures in columns (4) and (6) of Table III for the appropriate solvent.

Amyl alcohol, alone of the alcohols, does not show co-operating monomolecular spirals of the same sense (Table III). Accordingly this difference was tested in Table XII.

Finally a test was performed on the difference in proportions of bimolecular steps observed in the growth from xylene at various temperatures (Table XIII, page 122).

TABLE VI[+]

Step height difference between polar and non-polar solvents.

Standard; Xylene $N_o = 42$ $n_o = 17$ $p_o = 0.40$

	N	n	p	$p - p_o$*	P'	E	$\frac{p - p_o}{E}$	
Amyl acetate	53	2	0.04	0.36	0.20	0.08	4.5	SIG
Dioxan	31	0	0.00	0.40	0.23	0.10	4.0	SIG

[+]See note at bottom of next page

*Arithmetical value always taken

TABLE VII+

Step height difference between polar and alcohol solvents.

Standard: Amyl acetate: $N_o = 53$ $n_o = 2$ $p_o = 0.04$

	N	n	p	$p - p_o$	P'	E	$\frac{p - p_o}{E}$	
Iso-propyl	45	25	0.56	0.52	0.28	0.09	5.8	SIG
Propyl	65	24	0.37	0.33	0.22	0.08	4.1	SIG
Butyl	50	16	0.32	0.28	0.17	0.07	4.0	SIG
Amyl	54	0	0.00	0.04	0.02	0.03	1.3	INSIG

TABLE VIII+

Step height difference between individual non-polar solvents.

Standard: Xylene: $N_o = 42$ $n_o = 17$ $p_o = 0.40$

	N	n	p	$p - p_o$	P'	E	$\frac{p - p_o}{E}$	
Pet. ether	31	7	0.23	0.17	0.33	0.11	1.5	INSIG

TABLE IX+

Step height difference between individual polar solvents.

Standard: Amyl acetate $N_o = 53$ $n_o = 2$ $p_o = 0.04$

	N	n	p	$p - p_o$	P'	E	$\frac{p - p_o}{E}$	
Dioxan	31	0	0.00	0.04	0.02	0.03	1.3	INSIG

+NOTE: In Tables VI, VII, VIII, IX, X and XIII N (or N_o) is the number of crystals on which step heights have been measured (i.e. the value given in column (2) of table III, page 115). n (or n_o) is the number of crystals exhibiting bimolecular steps (i,e. the sum of the figures given in columns (6), (7) and (8) of Table III).

$p = \frac{n}{N}$, $p_o = \frac{n_o}{N_o}$, $P' = \frac{n + n_o}{N + N_o}$, $E = \sqrt{P'(1-P')\left(\frac{1}{N} + \frac{1}{N_o}\right)}$

A value of $\frac{p - p_o}{E}$ greater than 3 indicates a probability of less than 0.27% that the difference in results is due to a sampling error. Such values therefore indicate a statistically significant difference.

TABLE X[+]

Step height difference between individual alcohol solvents.

(a) Standard: Iso-propyl: $N_o = 45$ $n_o = 25$ $p_o = 0.56$

	N	n	p	$p - p_o$	P'	E	$\frac{p - p_o}{E}$	
N-propyl	65	24	0.37	0.19	0.45	0.10	1.9	?
Butyl	50	16	0.32	0.24	0.43	0.10	2.4	?
Amyl	54	0	0.00	0.56	0.25	0.09	6.2	SIG

(b) Standard: Butyl: $N_o = 50$ $n_o = 16$ $p_o = 0.32$

	N	n	p	$p - p_o$	P'	E	$\frac{p - p_o}{E}$	
Propyl	65	24	0.37	0.05	0.35	0.09	0.6	INSIG
Amyl	54	0	0.00	0.32	0.15	0.07	4.6	SIG

TABLE XI[*]

Two monomolecular spirals of the same sense : difference between non-polar and polar solvents,

Standard: Xylene: $N_o = 13$ $n_o = 0$ $p_o = 0.00$

	N	n	p	$p - p_o$	P'	E	$\frac{p - p_o}{E}$	
Pet. ether	8	2	0.25	0.25	0.10	0.13	1.9	?
Amyl acetate	17	16	0.94	0.94	0.53	0.18	5.2	SIG
Dioxan	2	2	1.00	1.00	0.13	0.25	4.0	SIG

TABLE XII[*]

Two monomolecular spirals of the same sense : difference between amyl and other alcohols.

Standard: Amyl alcohol: $N_o = 3$ $n_o = 3$ $p_o = 1.00$

	N	n	p	$p - p_o$	P'	E	$\frac{p - p_o}{E}$	
Butyl alc.	16	0	0.00	1.00	0.16	0.23	4.3	SIG

[+]See note at bottom of page 120.

[*]See page 119 for explanation of values of N, N_o, n, n_o in Tables XI, XII.

TABLE XIII[+]

Variation of step height with temperature.

Standard: Xylene at 20°: $N_o = 42$ $n_o = 17$ $p_o = 0.40$

	N	n	p	$p - p_o$	P'	E	$\frac{p - p_o}{E}$	
Xylene (40°)	26	3	0.12	0.28	0.29	0.11	2.5	?
Xylene (50°)	28	1	0.04	0.36	0.26	0.11	3.4	SIG

Interpretation of the analysis.

In cases where the value of $\frac{p - p_o}{E}$ is found to exceed 3, the result has been marked "SIG" in the tables to show that the difference is significant and cannot possibly be accounted for by a sampling error. Differences giving values of less than 1.9 have similarly been marked "INSIG". However this still leaves some results for which the difference is such that a value is obtained lying between 1.9 and 3. Such results have been marked with a query (?). The reason for this is that the boundary between significance and insignificance is not sharp. Thus a value of 1.9 means that there is still a 95% chance that the difference is not due to a sampling error. While this is far from being a statistical certainty, it still leaves a good chance that the difference is significant. Accordingly such differences will be described as "fairly significant".

It is now necessary to discuss the scientific importance of significant and fairly significant differences.

If the difference between two sets of results is shown to be significant then we may take this difference as a scientific fact. Accordingly theories may be built up using the fact that these results are different. On the other hand if the difference is only fairly significant it cannot be taken as a scientific fact, as there is still a 5% chance that the results are due to the randomness of the sampling. Thus we cannot build up theories using this difference as an established fact. However if our theory, based on scientific facts suggests a reason for these fairly significant differences, then we may take it that these differences tend to support the theory. Further than this we may not go.

Results of the analysis.

Tables VI, VII (pages 119-120) show that the three groups are significantly different with respect to the proportions of bimolecular steps.

Table VIII shows an insignificant difference between the individual non-polar solvents with respect to step heights. Table IX shows a similar difference between the individual polar solvents in this respect. Thus the step height results justify the division of the solvents into the polar and non-polar groups.

Table X shows a significant difference between amyl alcohol and the other alcohols in respect of step

height. The differences between the other members of the series are only fairly significant or insignificant. Thus the alcohol series differs from the other two groups and we are justified in dividing the solvents into the three groups as in Table III.

Table XI shows a significant difference between the polar solvents and xylene in respect of the number of crystals exhibiting two co-operating monomolecular spirals of the same sense. There is also a fairly significant difference between xylene and petroleum ether in this respect. Table XII shows a significant difference between amyl and butyl alcohols in this respect and we may take it that there are similar differences between the other alcohols and amyl alcohol.

Finally Table XIII shows a significant decrease in the proportion of bimolecular steps on increasing the temperature of crystallisation from xylene to 50°. However the decrease in proportion on increasing the temperature to 40° is only shown to be fairly significant.

(2) GROWTH OF 4-METHYLTRITRIACONTANE.

The crystals of this compound are generally fairly irregular in outline and do not appear to grow by spiral growth.

It is possible to observe small crystals which cannot have grown appreciably after nucleation. Much of this material is fairly thick suggesting that the nuclei of this compound are frequently much thicker than those normally encountered in the growth of long chain compounds. Plate XXXII (page 126) shows small crystals which are from five to ten molecules thick.

Plate XXXIII (page 126) shows an irregular crystalline layer with monomolecular growth layers on the surface. There is also evidence of island nucleation. This crystal shows traces of the surface folds which are characteristic of the crystals. These folds are better illustrated in Plate XXXIV (page 127). The folds vary in size from submolecular to multimolecular dimensions. It will be noted that they provide "anchor points" for the growth layers, many of which appear to originate at folds.

Over 100 crystals were studied and only three of these showed genuine spiral growth terraces. Two of these spirals are shown in Plates XXXIV and XXXV (page 127). They are very irregular in outline and approximate to a circular shape. Both spiral terraces form part of a long crystal lath. Such laths occur fairly commonly in the growth.

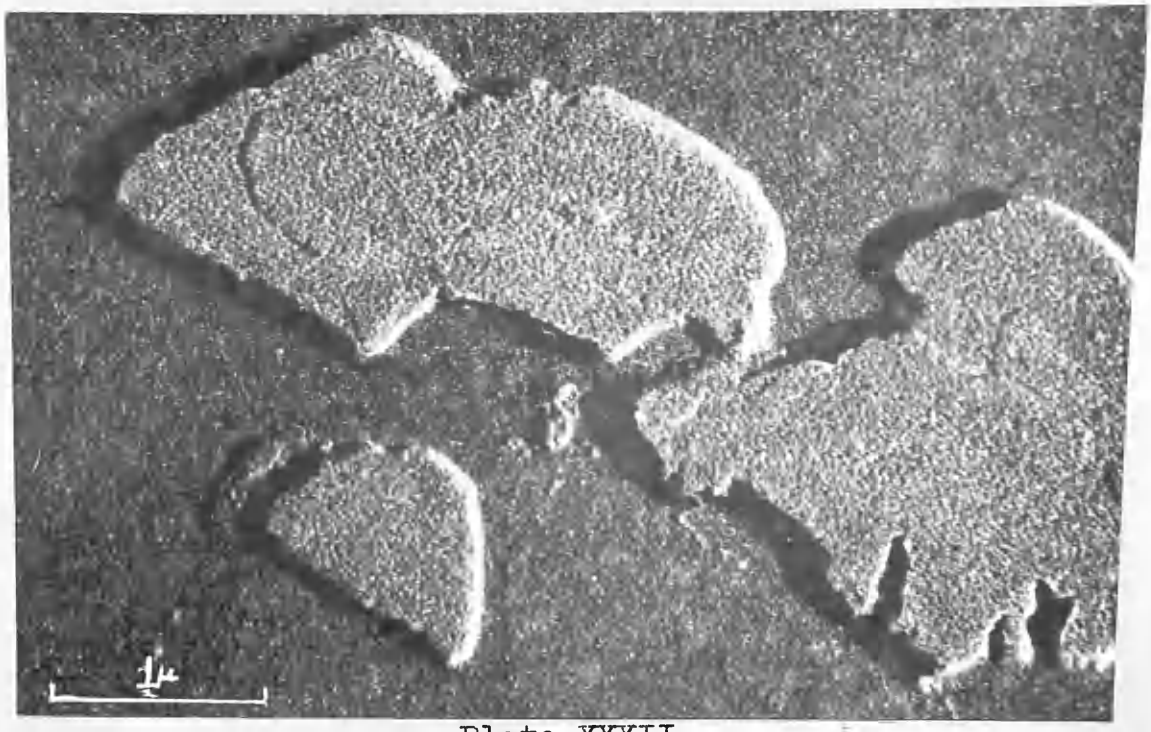

Plate XXXII

This micrograph shows small crystals of 4-methyltritriacontane with thicknesses varying from 5 - 10 molecules.

Plate XXXIII

This plate shows an irregular layer of methyltritriacontane with monomolecular layer growth steps. These crystals show traces of the characteristic surface "folds".

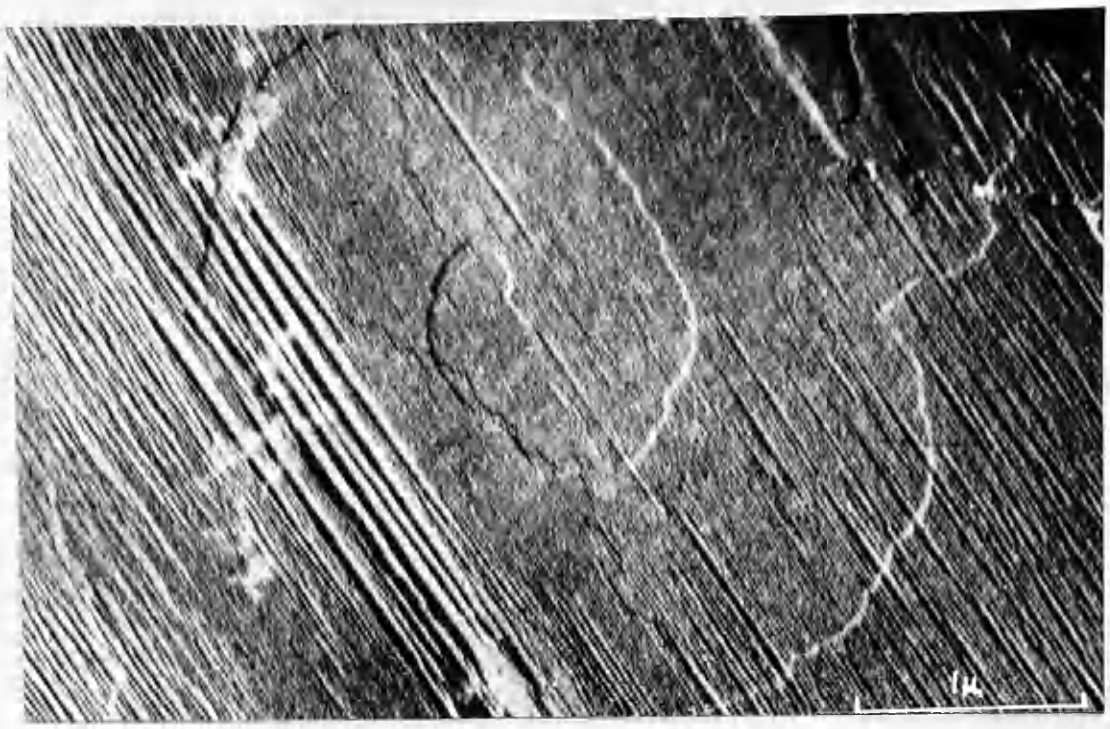

Plate XXXIV

This methyltritriacontane crystal provides a better illustration of the surface "folds", which provide anchor points for monomolecular growth layers. One of the three spirals observed is also shown in this micrograph.

Plate XXXV

This plate shows another spiral observed on a methyltritriacontane crystal. The surface folds are again visible.

The crystals are thus frequently elongated in one direction. Some crystals are observed to have an approximately hexagonal shape. These phenomena are similar to those which will be described for hexatriacontane crystals grown at high supersaturation.

The crystals grown at 55° (i.e. above the transition point) have in general a much more regular surface than those grown at room temperature. Fewer laths occur, the crystals generally being extended fairly evenly in all directions (Plate XXXVI, page 129). The surface folding appears to be absent or at any rate less pronounced. Growth again occurs by monomolecular layers, no spiral terraces being observed.

(3) GROWTH OF 4-METHYLTRITRIACONTANONE-26.

It was frequently observed that crystallisation of a drop of solution of this compound on a glass slide resulted in the formation of a few large crystals on the periphery and almost no crystals at all in the interior of the drop. Many of these crystals were roughly hexagonal in shape. This phenomenon persisted even when very dilute solutions were used.

Plate XXXVII (page 129) shows a silicon monoxide replica of such a crystal. It is fairly irregular

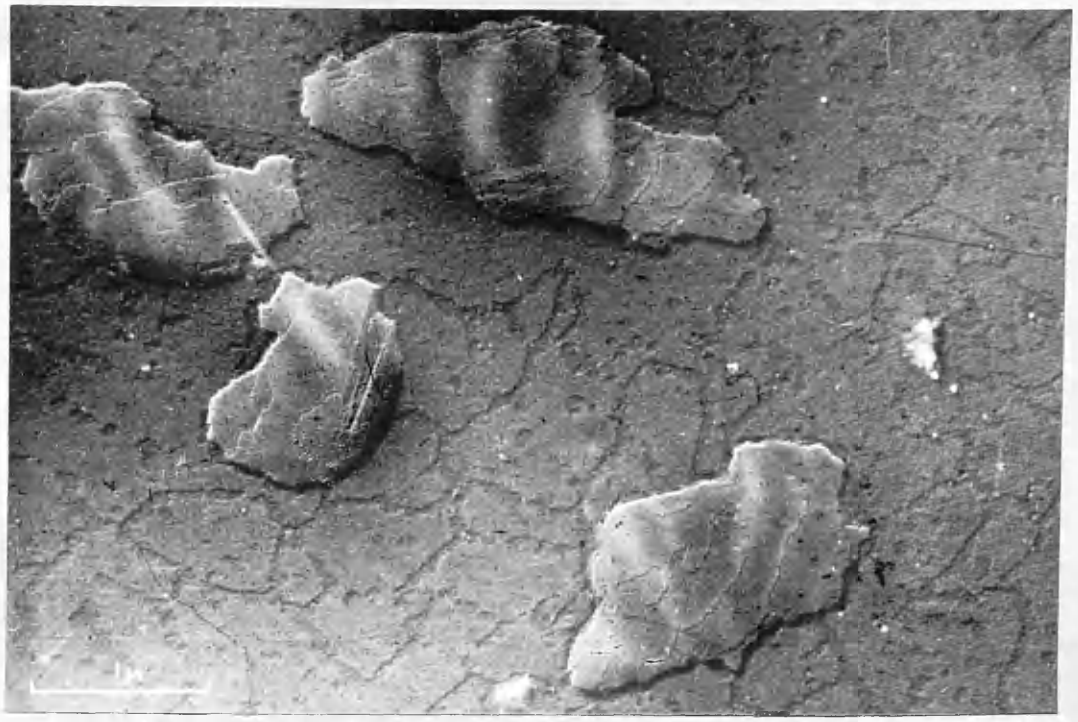

Plate XXXVI

This plate shows methyltritriacontane crystals grown at 55°. The crystals possess monomolecular growth layers but the surface folding is less marked.

Plate XXXVII

This micrograph shows a silicon monoxide replica of a methyltritriacontanone crystal possessing monomolecular growth layers.

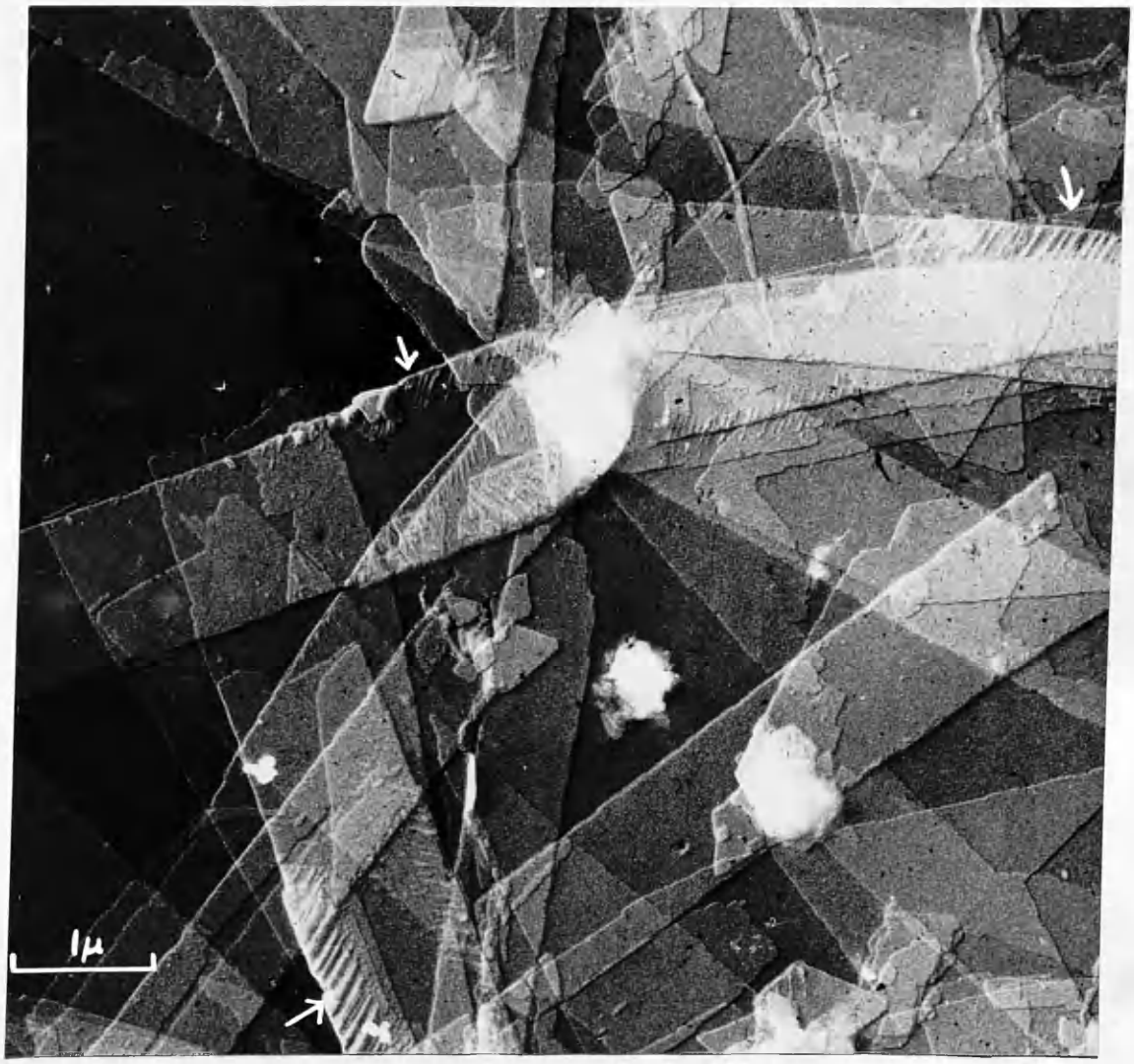

Plate XXXVIII

These crystals of n-propyl 18-keto-n-pentacontanoate show the characteristic twin laths exhibiting edge buckling.

in outline and possesses a large number of narrowly spaced monomolecular steps. There does not seem to be any of the surface folding encountered in the previous compound. Some of the crystals do appear to show large surface irregularities however.

(4) GROWTH OF 18-KETO-N-PROPYL N-PENTACONTANOATE.

The crystallisation of this compound from petroleum ether produces a large number of twinned laths. These frequently possess spiral growth terraces at various sites on the lath. There is evidence for edge buckling on some of the laths as shown on Plate XXXVIII (page 130).

Individual crystals possessing spiral growth terraces also occur. These frequently possess twist boundaries as described by Anderson and Dawson for the ester itself. Twist angles of 8°, 15°, 27°, 37°, 51°, and 67° were observed.* Twist through 67° (corresponding to the twinning angle was very common. Plate XXXIX (page 132) shows a crystal with a twist angle of 37°.

The crystals grown at high supersaturation exhibited twist boundaries to an even greater extent. There is also some evidence for growth by multimolecular layers in this batch. Thus Plate XL (page 132) shows a crystal which has grown by bimolecular layer growth.

*Plate XXXIX shows the difficulty of accurately measuring twist angles. Accordingly no great significance should be attached to the values quoted.

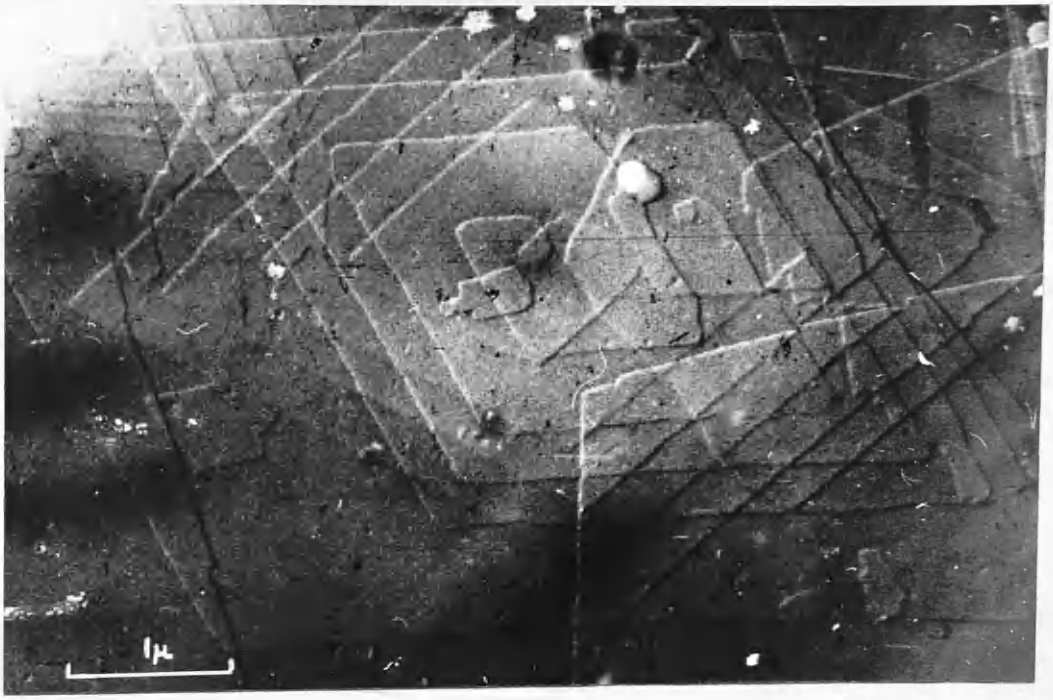

Plate XXXIX

This crystal of the keto-ester exhibits twist between the upper and lower surfaces. (Angle of twist 37°).

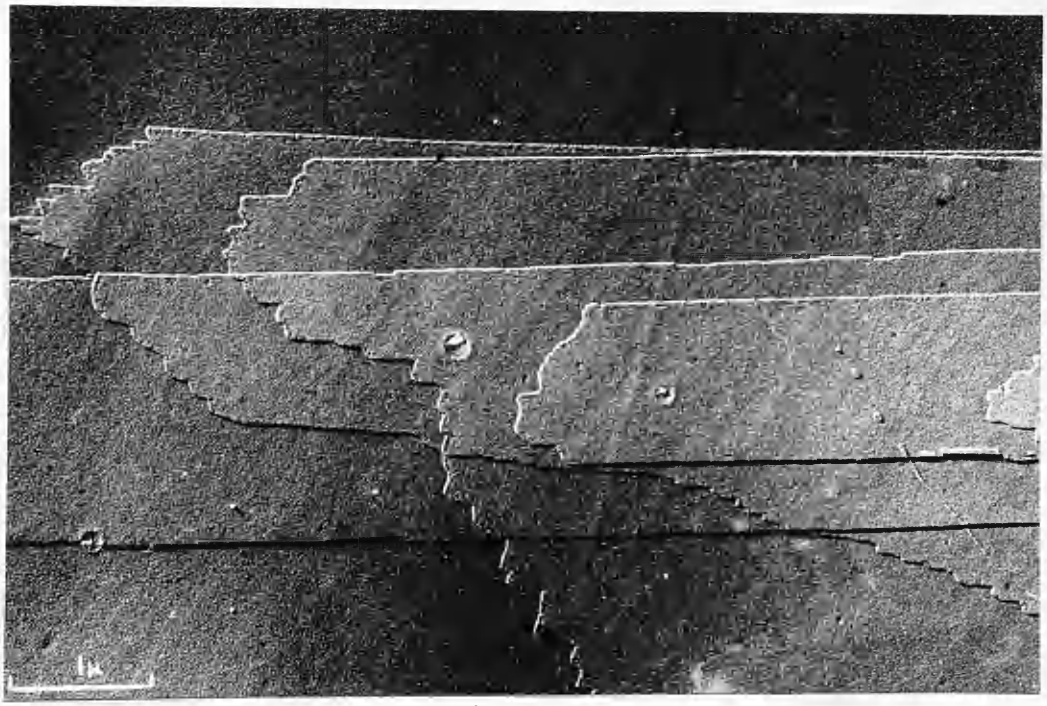

Plate XL

This plate shows a crystal of the keto-ester grown at high supersaturation possessing bimolecular growth layers.

(5) GROWTH OF IODOHENTRIACONTANE.

This compound gives extremely irregular crystals. These all exhibit a "grain boundary" effect (Plate XLI, page 134). This results in blocks of the crystals being out of alignment. The crystals are very rough in outline and also possess a rough surface. They appear to grow by monomolecular layer growth. There is no evidence of spiral growth.

(6) GROWTH OF IODOHENTETRACONTANE.

The crystals of this compound are much more regular than those of the previous one. The crystals grow by spiral growth, crystals with several dislocations being quite common (Plates XLIII, XLIV - page 135). There are indications of the occurrence of edge buckling in several instances (Plate XLII, page 134 and Plate XLIII). Many of the crystals show a surface irregularity similar to that encountered in the crystals of methyltritriacontane. In this case, however, the folds are nearly all submolecular the maximum height being of the order of 15A°. The folds are usually about 50 - 200 A° apart. At the edge they frequently appear to terminate in larger steps presumably the result of edge slip. This has just begun to occur on the crystal shown in Plate XLII. The effect is better shown in Plate XLIII, where steps of varying height have

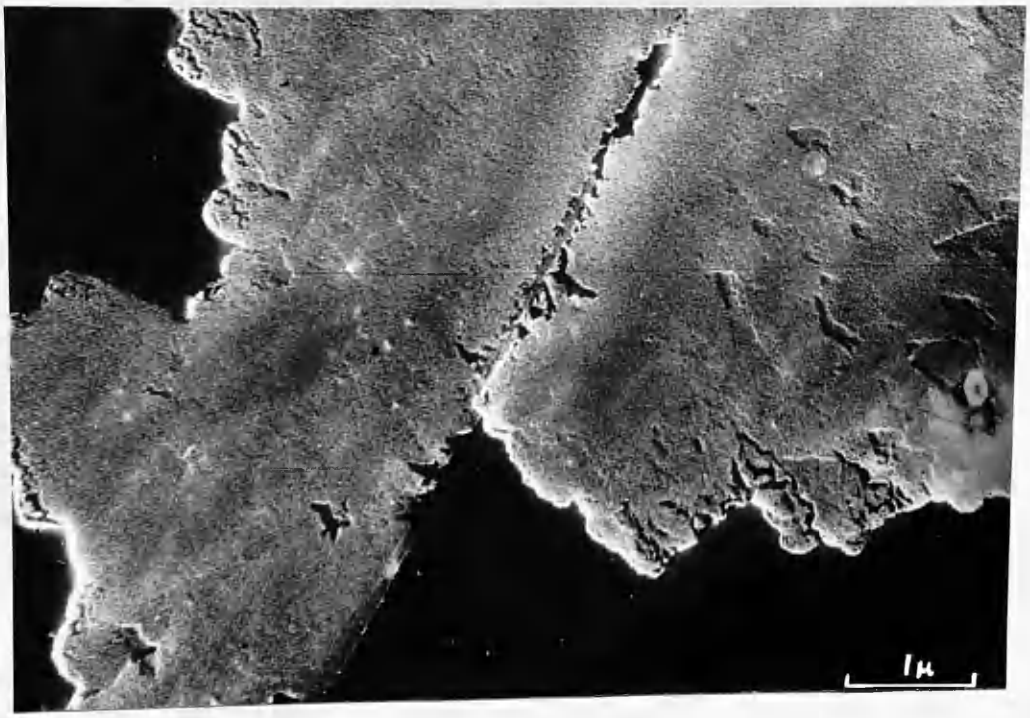

Plate XLI

This plate shows an iddohentriacontane crystal exhibiting irregular growth and "grain boundary" effect.

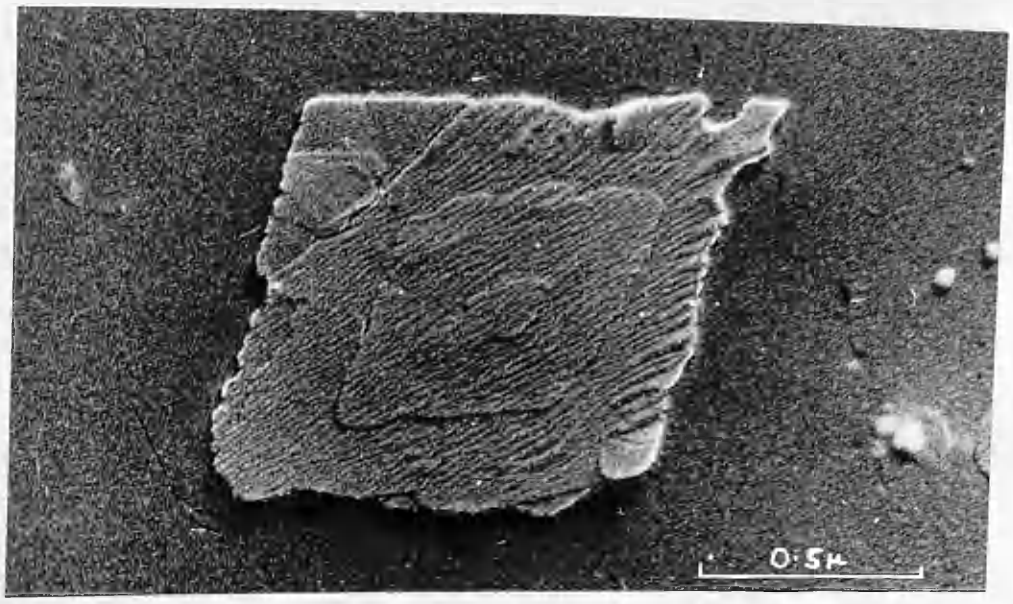

Plate XLII

This iodohentetracontane crystal shows the surface folds characteristic of the compound. Spiral growth occurs and the crystal shows signs of splitting at the top left hand corner.

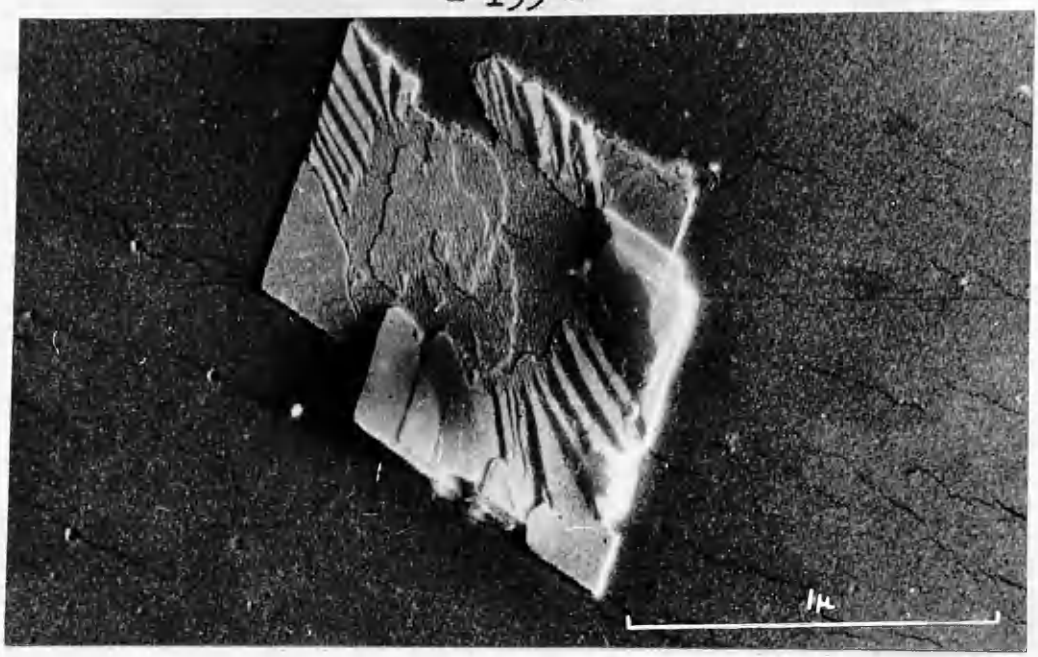

Plate XLIII

On this iodohentetracontane crystal edge buckling has produced steps of varying height. Some of the multimolecular steps at the bottom corner appear to have grown. Several monomolecular spirals are visible in the centre of the crystal.

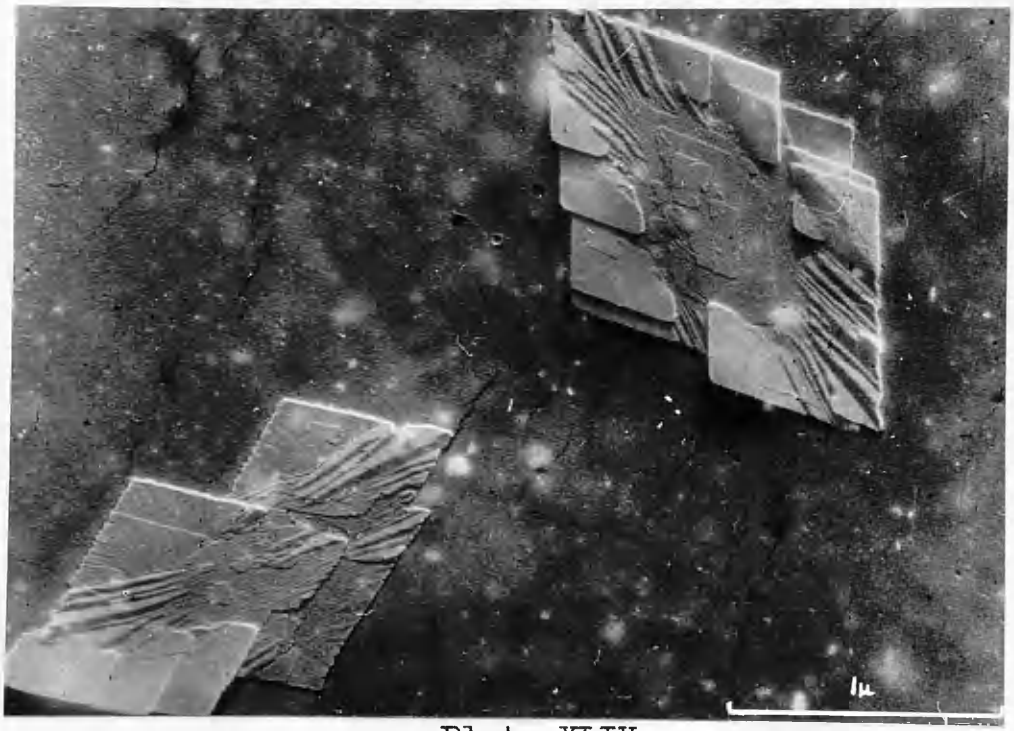

Plate XLIV

Extensive corner growth has occurred on these iodohentetracontane crystals. As a result the left hand crystal appears to have grown into another crystal.

been produced at the top left hand corner of the crystal. At the opposite corner growth has begun to take place on these steps - this is also shown in Plate XLIV, page 135.

There is evidence of the beginnings of monomolecular spirals at certain places on the crystals in Plates XLIII, XLIV but some of the multimolecular steps also appear to have grown. There is also evidence of extensive growth at the corners of the crystals shown in Plates XLIII, XLIV. This has occurred to such an extent on one of the crystals in Plate XLIV that it appears to have grown into another crystal at the corner.

The crystals shown in Plates XLII, XLIII also appear to possess a definite split at one corner.

The interfacial angle of the crystals is usually about 67°, although some of the crystals appear to have interfacial angles slightly greater than this (up to a maximum of 71°). However the irregular outline at the corners renders accurate measurement impossible.

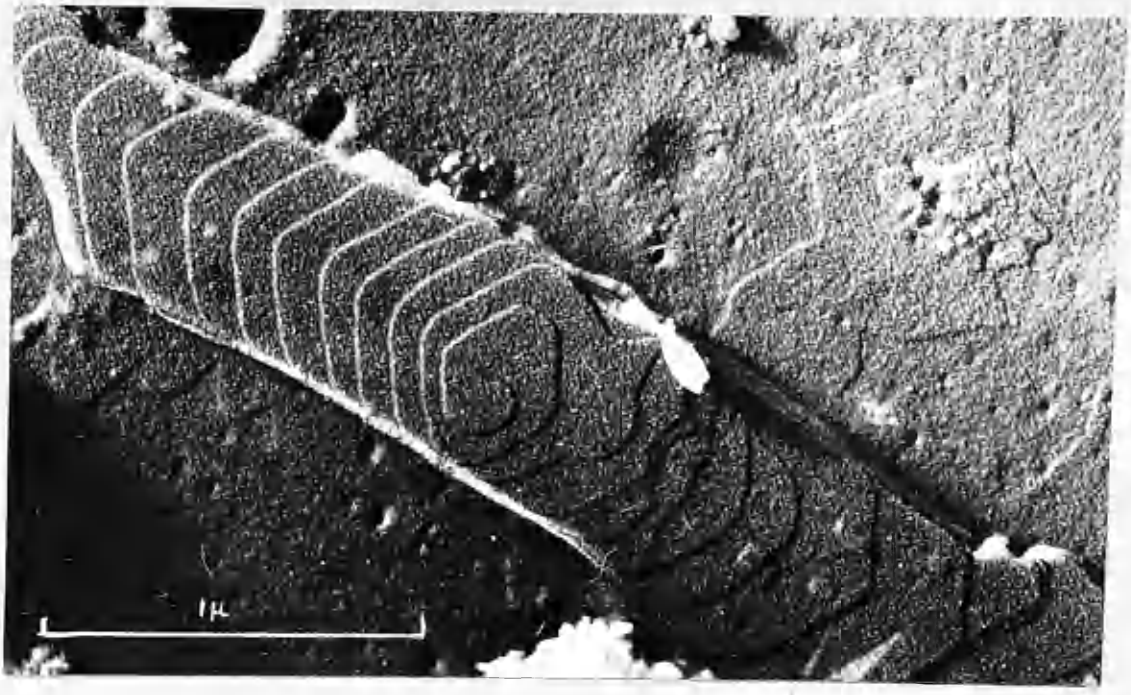

Plate XLV

This plate shows a needle like crystal of n-hexatriacontane grown at 100% supersaturation. It is extended in the direction of the obtuse corner of a normal crystal.

Plate XLVI

This hexatriacontane crystal grown at 100% supersaturation shows irregular lamellar growth at the edges.

(7) GROWTH OF N-HEXATRIACONTANE AT HIGH SUPERSATURATIONS.

Growth at 100% supersaturation.

In general it is found that the crystals in this batch grow by the spiral growth mechanism. There are, however some unusual features in the growth. Frequently needle like crystals with spiral markings are obtained (Plate XLV, page 137). These are usually fairly thick but lateral growth appears to have occurred preferentially in one direction. The outlines of the spiral terraces are fairly irregular, the corners being rounded. The steps on such crystals are invariably monomolecular.

Plate XLVI (page 137) shows the corner of a normal lozenge shaped crystal whose initial growth appears to have been by the spiral mechanism. At the edge however, there is evidence of irregular growth involving narrowly spaced molecular layers. These are generally monomolecular in height. Some multimolecular layers are observed among them but in many cases these appear to be the result of coalition of monomolecular layers.

The crystal in Plate XLVII (page 139) has a very irregular outline and some of the layers on its surface are multimolecular. These layers do not appear to have resulted from coalition of monomolecular layers and indeed cannot definitely be classified as growth steps. This crystal is also elongated in one direction.

Plate XLVII

This plate shows multimolecular growth layers on a hexatriacontane crystal grown at 100% supersaturation.

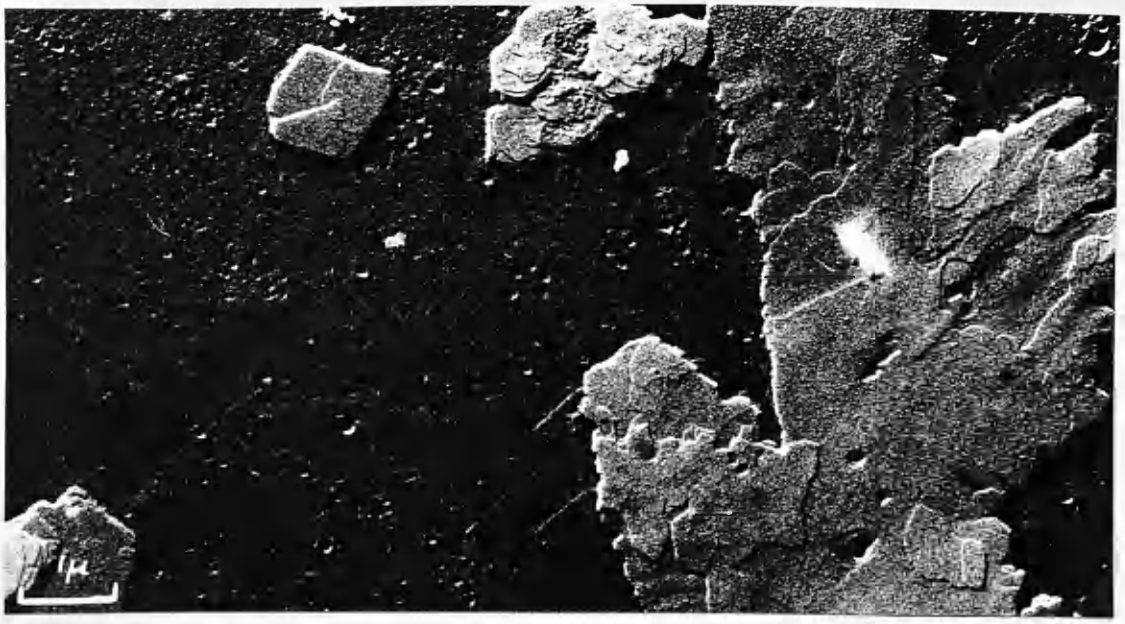

Plate XLVIII

These hexatriacontane crystals were grown at 50% supersaturation and exhibit monomolecular layer growth. Some of the crystals are hexagonal in outline.

Growth at 50% supersaturation.

In most respects the crystals grown at 50% supersaturation exhibit the same phenomena as those grown at 100%.

No needle like crystals are observed but crystals roughly hexagonal in form are occasionally present. These crystals frequently exhibit layer growth (Plate XLVIII, page 139). The layers are generally monomolecular although a few bimolecular layers are observed.

This crystallisation frequently produces crystals with a re-entrant edge (Plate XLIX, page 141). These invariably occur on crystals showing no trace of dislocations. The crystal shown in Plate XLIX possesses only one re-entrant edge, but crystals with two such edges also occur.

Most of the crystals in the batch, however, do grow by the spiral mechanism, the spirals resembling those on crystals grown at elevated temperatures in that they are irregular in outline. On the other hand, some of the crystals, particularly those which are hexagonal in shape, possess edges whose regularity is in marked contrast to the irregularity of the spirals described above.

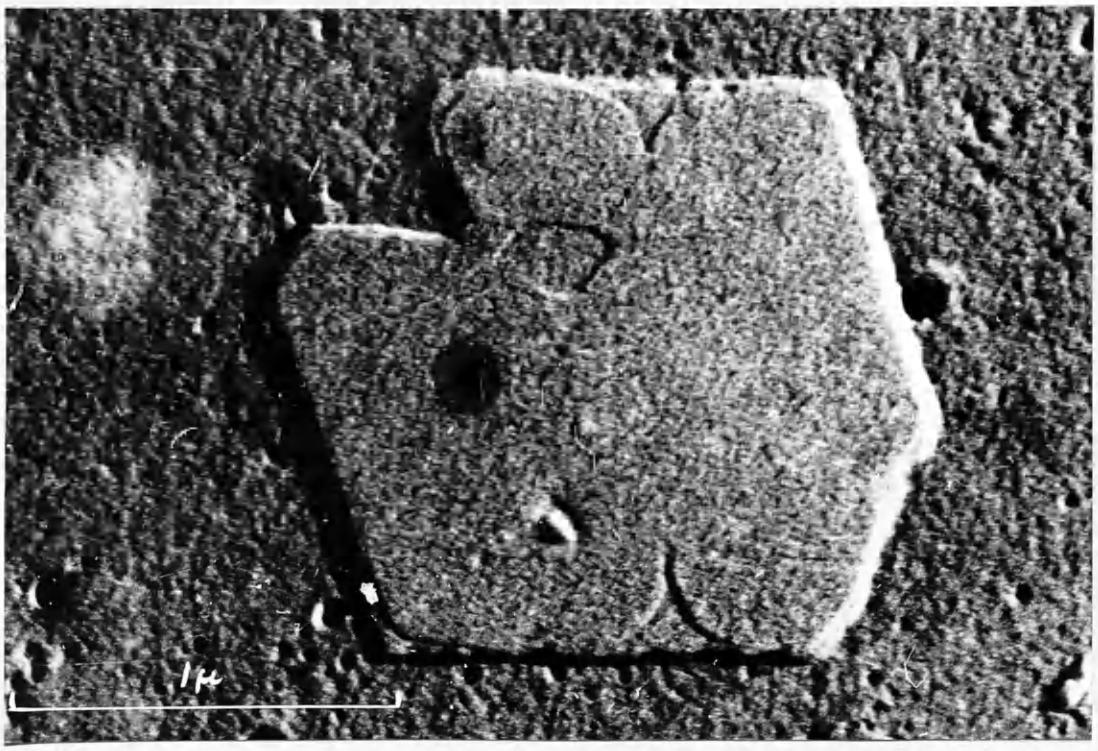

Plate XLIX

This hexatriacontane crystal grown at 50% supersaturation shows a roughly hexagonal shape with a re-entrant edge.

V - DISCUSSION

V - DISCUSSION

(1) STEP HEIGHTS

Only the step heights in the growth of n-pentacontanol are discussed here.

Step heights in growth from polar solvents.

The steps in the growth from polar solvents are predominantly monomolecular. A small number of bimolecular steps occur and the explanation of this lies in the fact that crystal growth is in some aspects a secondary process and will be influenced by the nature of the primary nucleus. Nucleation has some effect on the growth pattern of small crystals at any rate and this point will be discussed in section (6).

Most of the bimolecular dislocations tend to dissociate into two monomolecular spirals of the same sense. This dissociation will not be expected to occur in the growth from the non-polar solvents, when double molecules exist in the solution. The significant difference in the proportions of dissociating steps in the growth from polar and non-polar solvents is in accordance with this (Table XI, page 121).

Step heights in the growth from non-polar solvents.

The proportion of bimolecular steps in the growth from non-polar solvents is significantly greater than in the growth from polar solvents (Table VI, page 119).

This was to be expected in view of the presence of bimolecular aggregates in solution.

Most of the bimolecular dislocations do not dissociate into monomolecular spirals. However two small crystals grown from petroleum ether exhibited this structure. It is thought, however, that these are exceptional cases in which the rapid evaporation of solvent has affected the issue.

It might be anticipated that, since polymolecules exist in these solutions, some polymolecular steps should occur. However consideration of the structure of the polymolecules shows why none are observed. The molecules in such a polymer are packed with the chains parallel so that each can form a hydrogen bond with its two neighbours. Obviously the bimolecular form could equally well exist in a chain form, with the molecules packed head to tail, without violating the sterical conditions for hydrogen bonding. This type of complex results in the occurrence of bimolecular steps.

It is however impossible to form complexes of greater size, which have the chains arranged in this manner. Since only such a form will give rise to polymolecular steps, clearly the absence of such steps is still consistent with the relationship between step height and the type of structural unit present in solution.

Step heights in growth from alcohol solvents.

The alcohol solvents were originally selected as polar solvents. However the results show a significant difference, in terms of step height, from the polar solvents (Table VII, page 120).

A reconsideration of association phenomena suggests an explanation for this. Wolf, Dunken and Merkel (1940), Hofmann (1943) and Rao (1945) have all accounted for the non-association of alcohol molecules in polar solvents by their preferential association with solvent molecules. If we consider the alcohols as polar solvents, association will occur between solute and solvent molecules. However in this case the solvent molecule is capable of undergoing further association. Thus we may presume that on occasions it forms a hydrogen bond with a second solute molecule giving what may be described as a "pseudo-double molecule". The presence of such aggregates in the solution will reconcile the observed results with the step height hypothesis of Anderson and Dawson (1953). Such a reconciliation is necessary since we may take it that the hypothesis has received adequate support from the results obtained in the growth from non-polar and polar solvents and especially by the observed variation of step height with temperature, which is discussed on page 146.

There is a significant difference in the step height results obtained with amyl alcohol as compared with

the other members of the group, in that no bimolecular steps are observed (Table X, page 121). To account for this we must first consider the properties of a pseudo-double molecule which takes part in crystal growth.

The solvent molecule must be fitted into the lattice in the initial stages of growth at any rate. Whether it is retained as alcohol of crystallisation or not is uncertain. If the solvent molecule is too large to fit into the lattice then the pseudo-double molecules will be unable to partake in growth even if they are present in the solution. The observed absence of bimolecular steps would thus be related to the size of the amyl alcohol molecule. It does seem reasonable to suppose that whereas the lower alcohols can fit into the lattice, the amyl alcohol molecule cannot.

Table X shows differences between the other members of the group which are fairly significant or insignificant. It is believed that iso-propyl alcohol is more readily associated than n-propyl alcohol which is in turn more readily associated than n-butyl alcohol (Hofmann 1943), although the exact effect of increasing chain length is not exactly clear (Wolf, Dunken and Merkel 1940). However it is likely that there will be a small decrease in association with increasing chain length. Accordingly we might expect the proportion of bimolecular steps to decrease on proceeding from iso-propyl to n-propyl to butyl alcohol. If the differences are slight the low statistical significances are to

be expected. Further the difference between iso-propyl and the n-alcohols in this respect would be expected to exceed the difference between the two normal alcohols. The insignificant difference between the proportions of bimolecular steps in the growth from the two normal alcohols is thus consistent with this as is the fairly significant difference between the iso and n-alcohols.

It is of interest to note that only on crystals grown from amyl alcohol solutions is dissociation of bimolecular steps observed. This is in accord with the results of the growth from polar and non-polar solvents, in which dissociation was a common occurrence when no double molecules were present.

Effect of temperature on step height.

Table XIII (page 122) shows that there are significantly fewer bimolecular steps in the growth from xylene at an elevated temperature. This result is to be expected in view of the known decrease in association with temperature. The results show only a fairly significant difference in this respect between the crystals grown at 20° and those grown at 40° but the difference between those grown at 20° and at 50° is significant. These results provide further conclusive evidence in favour of the step height hypothesis of Anderson and Dawson (1953).

(2) FORMATION OF SCREW DISLOCATIONS.

Mechanism of dislocation formation.

The results of Anderson and Dawson (1955) showed that as far as long chain compounds were concerned, screw dislocation formation was an edge process, rather than a buckling process caused by irregular distribution of impurities. The observation of edge irregularities in crystals of the keto-ester (Plate XXXVIII, page 130) and iodohentetracontane (Plates XLII, XLIII, XLIV - pages 134-5) tends to confirm this. The crystal of pentacontanol in Plate XXI (page 103) also shows formation of screw dislocations at the edge of a crystal.

There still remains some doubt as to the exact nature of the process. It could be due to a fault in the stacking at the edge of the crystals as suggested by Anderson (1954) or an edge slip process as proposed by Anderson and Dawson (1955).

It is known that some bimolecular layers are formed in the growth from amyl acetate, since two bimolecular layers and several twins have been observed. However the layer must necessarily be built up from single molecules as no double molecules exist in these solutions. Now since bimolecular spirals or two monomolecular spirals of the same sense are observed on many crystals, some of these bimolecular layers must give bimolecular dislocations. If, however, dislocations are produced by a stacking fault

only monomolecular dislocations could result. Thus this mechanism fails to explain the existence of bimolecular dislocations on crystals grown from amyl acetate. Conversely the edge slip mechanism presents no difficulties in this direction.

On the other hand the results tabulated in Table III (page 115) tend to suggest that there are more bimolecular layers formed in the growth from amyl acetate than from dioxan. That this difference is fairly significant is demonstrated in Table XIV (a value of 2.6 means that there is a probability of less than 1% that the difference is due to random sampling.).

TABLE XIV

Difference between polar solvents in bimolecular layer formation.

Standard: Amyl acetate: $N_o = 53$ $n_o = 17$ $p_o = 0.32$

	N	n	p	$p - p_o$	P'	E	$\frac{p - p_o}{E}$	
Dioxan	31	2	0.06	0.26	0.23	0.10	2.6	?

(In this table n (or n_o) represents the number of bimolecular layers formed and is found by adding the figures in columns (4) and (6) of Table III.)

It is considered that this difference is due to the fact that the monomolecular layers formed from dioxan give rise to dislocations fairly readily and thus give rise

to growth by monomolecular spirals. However in the growth from amyl acetate if dislocations are not formed very readily , then there is a possibility of addition of a second layer before a dislocation is formed. Hence if we can explain why dislocations should be less readily formed in monomolecular sheets from amyl acetate, then we can account for the greater number of bimolecular layers formed in this instance.

The stacking fault theory provides the required explanation. If a molecule adds in a position out of register, then it may shift to the position of register by subsequent slip. If however the next molecule adds on before this can occur then the molecule has less chance of slipping back and may be trapped in an out of register position. The stacking fault is thus permanent and a dislocation can be formed. The more rapidly the subsequent molecules add on, the more likelihood there is of molecules being trapped. In other words the more rapidly the solvent evaporates the greater chance there is of a stacking fault and dislocation occurring.

Thus the stacking fault theory can account for a case which is only explained by the edge slip mechanism if we can introduee a relationship between slip and surface tension of the solvent. The fairly significant difference in Table XIV thus provides evidence which tends to support the stacking fault theory.

So far, then, we have quoted two lines of evidence which apparently lead to contradictory conclusions. However, it is possible that dislocation formation is a two stage process involving both stacking faults and edge slip. On this basis we assume that stacking faults occur and that these then facilitate edge slip to produce dislocations. Such a mechanism would be consistent with both the arguments quoted above. It will be shown that evidence from structural considerations tends to support the two stage mechanism.

The alignment of the spiral centres with the twin boundary in the crystal of Plate VIII (page 90) is of interest in connection with this theory. The twin boundary may be regarded as a line of stacking faults along which slip may readily occur to produce dislocations.

Structure effects on dislocation formation.

It is observed that the keto-ester forms screw dislocations very readily as very small crystals frequently exhibit spirals. Further many of the crystals exhibit the edge buckling effects which are thought to indicate the genesis of dislocations. This can be accounted for on the basis of the two stage process discussed above.

The keto-group and possibly the fairly large end group will probably lead to a stabilisation of stacking faults in crystals of this compound. In other words if

a molecule enters the lattice in a position of non-register it is likely to remain there. Consequently edge slip can occur readily and there will be a chance of dislocations being formed. In other words a crystal does not need to attain a very large size before a dislocation is formed. Once it has been formed, subsequent growth will lead to thickening of the crystal by spiral growth rather than to lateral extension of the crystal.

In the side chain compounds very few dislocations are observed, although the argument outlined above would lead us to suppose that stacking faults will occur to an even greater extent in these compounds owing to the size of the side chain. Indeed the occurrence of surface folds on the crystals provides evidence in support of this supposition. However it is considered that the methyl side chain is of such a size as to impede edge slip and dislocation formation is thereby rendered very difficult. Thus side groupings in the chain enhance the production of stacking faults but can only lead to readier dislocation formation if their steric effect is too small to interfere with edge slip which comprises the second part of the process of dislocation formation.

Thus of the two structural factors so far discussed, one is considered to affect the stacking and the other edge slip. If, then, we do not have a mechanism involving both, we must postulate that dislocations are

formed in two distinct fashions. This is of course possible, but the above mechanism of general application appears to give the better explanation.

The phenomena encountered in the iodide crystals can also be accounted for on the basis of this mechanism. In the iodide, $C_{31}H_{63}I$, the molecules pack with the iodine atoms together (Ställberg, Ställberg-Stenhagen and Stenhagen 1952), whereas in the iodide $C_{41}H_{83}I$ they pack with the iodine atoms adjacent to a hydrocarbon end group. The presence of a large end group will favour the occurrence of stacking faults in both compounds. However, in the first compound it is considered that the concentrated arrangement of the iodine atoms will prevent slip and thus no screw dislocations are formed. In the second compound however, dislocations can result from slip, since the iodine atoms are not comcentrated in such a small volume and there is not such a large energy barrier opposing slip. The presence of a large number of stacking faults in this compound will thus result in the occurrence of a large number of screw dislocations as is experimentally observed.

The effects of large end groups on growth and the significance of the large number of stacking faults in these compounds are discussed in section (3).

Temperature effect on dislocation formation.

The pentacontanol crystals grown from xylene at temperatures greater than 60° show no trace of spiral

growth and it is deduced that the conditions are unfavourable to the formation of screw dislocations at this temperature.

It is known that an energy barrier which is insurmountable at room temperatures may occasionally be quite easily traversed at higher temperatures. The rate of conversion of a crystal containing a dislocation to a perfect crystal may be expressed as a function of $e^{-E/RT}$ (where E is the activation energy of the conversion). It is seen that if T is increased so is the rate of conversion. Thus the structure containing a dislocation becomes less stable at higher temperatures owing to the thermal fluctuations of the molecules. It is readily seen that temperature can affect both the stacking and slip processes in this way.

Conclusion

From the above considerations it can be seen that there is still considerable uncertainty as to the mode of dislocation formation. This is primarily due to the fact that growth occurs on a dislocation immediately it is formed and hence the observation of dislocations as such is impossible. A secondary factor is that investigation of the processes leading to formation of dislocations requires resolution on a sub-molecular scale, which is not at present available. However the results have rendered it possible to propose a tentative mechanism for the process.

(3) STRUCTURAL EFFECTS ON GROWTH.

(a) EFFECT OF SIDE CHAINS.

Nucleation.

The growth patterns observed on crystals of methyl tritriacontane strongly resemble those on hexatriacontane crystals grown at high supersaturation. Thus the crystals tend to be extended in one direction (Plates XXXII - XXXV, pages 126-7). Further some of the crystals exhibit a roughly hexagonal shape similar to that shown in Plate XLIX (page 141), for crystals grown at high supersaturation. In addition the spirals shown in Plates XXXIV and XXXV show the circular shape characteristic of high supersaturation growth.

The fact that growth occurs at higher supersaturation than normal is accounted for by the absence of screw dislocations on nearly all the crystals. Since spiral growth cannot readily occur, growth must of necessity take place at higher supersaturation in order that renucleation may be effected. (It should be noted that the experimental method of evaporation allows growth to occur at whatever supersaturation may be necessary. If a higher supersaturation is required for growth, then more solvent evaporates before initiation of crystallisation.)

There is, however, evidence that formation of the three dimensional critical nucleus takes place at higher supersaturation, since crystals not much larger in size

than the critical nucleus are observed with thicknesses of between five and ten molecular layers (Plate XXXII, page 126). This is probably due to the presence of the side chain prejudicing the formation of an ordered structure. The side chain upsets the linearity of the molecule and does not allow regular packing of the molecules. The orientation effect of the side chain thus causes the formation of a disordered structure, which is less stable since molecules can more readily dissolve from it. Thus nucleation necessitates a higher ~~critical supersaturation~~ concentration and production of a larger critical nucleus to counteract this effect.

The preferential growth at the edge of the drop of solution in the case of the ketone can also be related to the supersaturation required for nucleation. The critical supersaturation will first be attained at the drop edge and nucleation will commence, entailing removal of material from solution. Diffusion will occur from the centre of the drop to compensate for this loss of material and growth will continue on the nuclei already formed. Eventually so much material will have diffused from the centre of the drop that the critical supersaturation will probably only be attained with difficulty in this region. There is thus little crystallisation in the centre of the drop. In the normal case the critical supersaturation is not so high and evaporation of solvent will result in the critical

supersaturation being achieved at the centre of the drop before an appreciable amount of material has diffused outwards.

Crystal structure of methyl substituted paraffins.

This difficulty in achieving regular packing is responsible for the surface folding effect shown in Plates XXXIII, XXXIV and XXXV (pages 126-7). The molecules require a larger packing volume in the lattice, yet the lattice dimensions are approximately the same as in the normal hydrocarbon. If however the molecules are packed in some form of corrugated arrangement, it is possible for each molecule to have the packing volume it requires without affecting the lattice dimensions. In effect this means that the positions of the side chains across the crystal are staggered. Presumably the original packing results in a disordered structure which buckles or folds to give the more ordered corrugated structure, which is still far from being an ordered structure in the normal sense of the word.

It is interesting to note in this connection that the intensities of the high order X-ray reflections for the methyl hydrocarbon fall off rapidly and that Ställberg-Stenhagen and Stenhagen (1948) attribute this to disorder in the vertical direction.

Above 55° the methyl hydrocarbon undergoes transition to a tilted chain form. Since there is less evidence

of folding in these crystals it is presumed that packing is more easily performed in this lattice. Ställberg-Stenhagen and Stenhagen found that the 2-methyl hydrocarbon, which crystallises at room temperature in a tilted chain form, gives a good X-ray powder pattern, suggesting an ordered structure. This observation is thus in agreement with the evidence adduced here for better packing in the tilted chain form.

Growth

As stated above growth will occur by two dimensional nucleation. This process will occur more readily as a result of the surface folding which will, in effect, produce a rough surface. Thus possibly two dimensional nucleation will occur at supersaturations less than those normally required for long chain compounds. However since three dimensional nucleation requires a higher supersaturation, the growth will still exhibit the phenomena associated with growth at high supersaturation.

Growth at high supersaturation would normally be expected to result in multimolecular lamellar growth on occasions. Thus one of the layers in Plate XXXIII (page 126) is bimolecular and layers of greater thickness have been observed.

The assistance given to two dimensional nucleation by the surface folds explains the anchoring of layers at folds as in Plate XXXIV (page 127).

This anchoring of layers behind the folds often results in layers terminating in the crystal interior(Plate XXXIV). However this does not necessarily entail the presence of a screw dislocation, since the termination of the molecular layer in the crystal is not anchored. Thus the layer can extend itself by further growth, unlike a spiral layer which cannot extend itself into the crystal by virtue of the spiral arrangement of the molecules at the dislocation centre. No such molecular arrangement exists at the ends of the layers in this case.

(b) EFFECT OF LARGE END GROUPS

The contrast between the growth of the two iodides is consistent with the difference in long axial repeat period reported by Ställberg, Ställberg-Stenhagen and Stenhagen (1952). As shown earlier the structure of the iodide, $C_{31}H_{63}I$, is unfavourable to formation of screw dislocations (page 152). Further, growth will involve migration of an iodide end group over a similar end group surface, which is likely to be extremely difficult. The "grain boundary" effect observed on these crystals is likely caused by bad packing resulting from the close concentration of iodide end groups. The structure thus accounts for the extreme irregularity of the crystals observed.

The iodide $C_{41}H_{83}I$ is likely to form screw

dislocations readily from the considerations of section (2), page 152. Correspondingly the crystals do show fairly large numbers of dislocations despite their small surface area.

The surface folding on these crystals could either be due to a primary packing effect or to secondary folding of the lattice. Since the folds have heights of up to 15A° and are separated by distances of at least 50A° it is rather unlikely that they are caused by a primary packing effect. It is presumed that they are produced by folding in a similar manner to the folds in the branched chain compounds. Presumably in the close packed directions the large end group prevents the molecules achieving positions of compete register. Now in long chain compounds most of the growth takes place in the direction of the corners - i.e. in the two least close packed directions in the basal plane. Now although no a and b-axial measurements are available for this compound, it is presumed from the geometry of the crystals that the a-axis is appraciably longer than the b-axis (by a factor of the order of 1½). Thus it is likely that molecules adding in the direction of the a-axis could enter in positions of complete register, while those adding in the direction of the b-axis cannot. Thus there is a regular arrangement in the direction of the a-axis and an irregular arrangement in the b-axial direction. Such an arrangement is consistent with the packing described

above since it involves an irregular corrugated surface in the b-axial direction but a regular surface in the a-axial direction. The folds appear to be related indirectly to the primary packing arrangement.

Presumably the folding results in a magnification of the original packing defects. It is not clear why this folding should occur unless it results in a process whereby a completely random packing is converted to an arrangement in which the packing is regularised over small areas of the crystal, which are however out of register with each other.

It is expected that the original packing of this compound will not be so irregular as that of the side chain compounds and hence the subsequent folding is not so great.

Since edge slip can occur in these crystals, extensive slip will occur at the termination of the folds on the crystal edge. We may regard the folds as providing sites where slip has in actual fact begun. (It is also possible that slip may occur other than at the edge. This would account for the "split" visible on the crystals of Plates XLII, XLIII - pages 134,135) Thus many dislocations will be produced in the crystal and further multimolecular slip will be possible. In the normal paraffins with smaller stacking faults it is generally thought that slip cannot readily occur after thickening of the monomolecular sheet. Here, however, the large and extensive stacking faults will render multimolecular slip possible. Thus multimolecular

~~dislocations~~ steps are produced on the crystal edge. From the previous results such ~~dislocations~~ steps would be expected to dissociate. Such dissociation has however occurred on extremely few of the crystals. Since dissociation only occurs by virtue of migration providing more molecules at the bottom of the step, restricted migration could account for lack of dissociation. Such a restriction will very likely be imposed by the surface folds and also by the iodine end group. Growth on the steps will probably occur by direct condensation and so there is no reason why dissociation should take place.

The restrictions imposed on migration by the surface folds also account for the extensive growth at the acute corners. Migration can still occur down the "channels" between folds (subject to the effect of iodide end groups) so that there will be appreciable growth, in the direction of the fold axes i.e. in the direction of the acute corners. In the direction normal to the fold axes surface migration will be severely limited by the folds and consequently growth at the obtuse corners will be greatly curtailed.

The other outstanding problem in connection with this compound is its crystalline structure. Ställberg, Ställberg-Stenhagen and Stenhagen (1952) report tilted chains for this compound, which would be expected to result in a monoclinic structure. The interfacial angle is however very close to that for the orthorhombic form. The

only possible explanation is that the folding has resulted in diminution of the interfacial angle. This would account for the fact that some of the crystals possess angles up to 71°.

Thus large end groups and side chains not only modify growth considerably but also have an appreciable effect on the crystalline packing. The lattice arrangement in compounds with such groupings can no longer be regarded as the regular array characteristic of the normal crystal.

(4) THE EFFECT OF AQUEOUS SOLVENTS AND TEMPERATURE ON THE POLYMORPHISM OF PENTACONTANOL.

Effect of water on growth.

The results with aqueous and dry solvents prove conclusively that the hexagonal form with the additional edges is only obtained when the solvent contains moisture. This effect is clearly not a supersaturation growth effect since the additional edges increase in length towards the periphery in the same proportions as the normal edges. Further the crystals grown from a solution containing a very small quantity of water (Plate XXIII, page 105) only show the additional edges to a very small extent and then only in the outermost (i.e. first formed) layers. This suggests that water is removed from solution as the crystal grows and that the layers formed at the end of the crystallisation grow in a non-aqueous medium and consequently do not exhibit the additional edges. It is therefore concluded that water molecules are incorporated in the crystalline lattice. The water would be removed in the shadow-casting process which involves maintaining the specimens in a vacuum of 10^{-5} millimetres of mercury. The crystals grown from a very aqueous solution (Plate XVIII, page 101) have an extremely rough surface as would be expected if an appreciable quantity of water was pumped out from the crystals. The corners of the spiral steps are rounded on this crystal probably because the high water content of the

solution gives a precipitation effect in the later stages of growth and hence effects characteristic of high supersaturation growth. (The differential rates of evaporation of alcohol and water will lead to an aqueous enrichment of the solution as growth proceeds.)

If the structure of the paraffin type lattice (Fig. 8, page 165) is studied it is seen that an irregular hexagon can be picked out (ABCDEF). If a slight change could be made in the intermolecular distances in the pentacontanol lattice, a form with hexagonal symmetry could be produced, providing the chains were originally vertical. The incorporation of water molecules in the lattice could effect the small changes necessary for the transition. The lattice would then possess hexagonal symmetry, the water molecules forming hydrogen bonds with the alcohol molecules nearest them. The lattice dimensions of the substance are such as to allow this to occur. It is probable that were pentacontanol to exist in a tilted chain (B) form as would be expected for an even chain alcohol, it would not give hexagonally formed crystals in this manner.

It should be noted that of all the solvents used in this investigation only the alcohols are capable of dissolving water to any extent. This is the sole reason for the apparent specificity of the effect to the alcohol crystallisations.

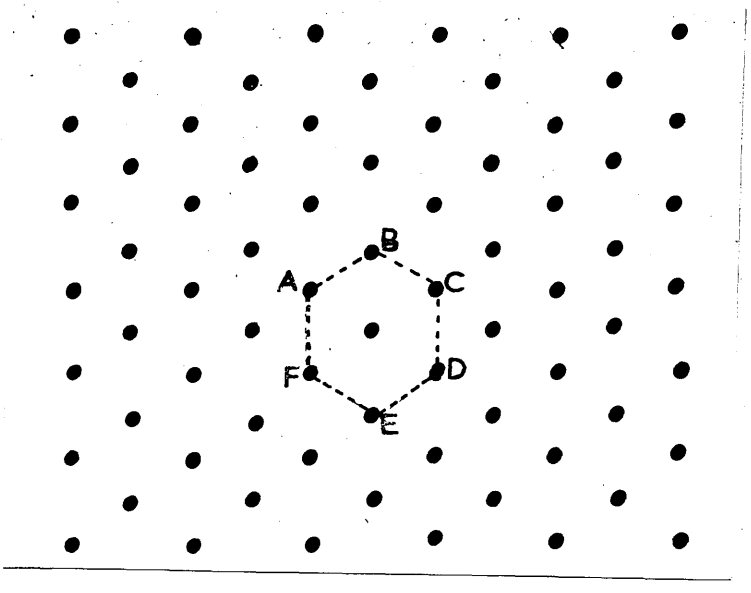

Fig. 8

Diagram of paraffin type lattice showing irregular hexagon ABCDEF.

The crystals exhibiting the additional edges are in fact likely to be mixed crystals of the hexagonal and orthorhombic forms with the latter predominating in most of the instances quoted. It is not surprising in view of this that most of the additional edges are rough in outline, since there may be local deficiencies in the number of water molecules which will result in a tendency towards formation of the normal form at various points along the edge.

Since this section of the work was completed, Jacobson (1953) has reported a hexagonal crystalline form for the nucleic acids. He accounts for this by the incorporation of water molecules in the lattice. He gives a slightly different interpretation of the role of water in the lattice. He uses the concept of the liquid water lattice introduced by Forslind (1952). According to this the molecules in liquid water are arranged in a pseudo-hexagonal lattice. Jacobson states that in the nucleic acid crystals, water molecules are attached to the acid chains by hydrogen bonds with the hydroxyl groups. These molecules are arranged in the form of the water lattice with which the acid molecules are aligned.

The results with the pentacontanol crystallisation could possibly be accounted for by the existence of a water lattice between the hydroxyl groups of two alcohol sheets. However, the nucleic acids provide sites for hydrogen

bonding along the entire length of a helical chain (Watson and Crick 1952), in contrast to the alcohols which only possess such sites at the chain ends. Further it would be difficult to reconcile the existence of such a lattice with the occurrence of bimolecular steps on many of the crystals exhibiting this structure.

It is of interest to note that Williams (1952) and Liquier-Milward (1953) both report the existence of a hexagonal form in electron microscope studies of dried nucleic acid crystals. This is consistent with our observation that the hexagonal form persists after all the water has been removed in shadowcasting. The result is to be expected since the molecules in the lattice cannot shift even after all the water molecules have been removed.

Effect of temperature.

Presumably the small changes in the lattice parameters can also be effected by the energy available at high temperatures. This would account for the occurrence of a hexagonal form in crystals grown near the melting point and also for the observation of this form among crystals grown from xylene at elevated temperatures.

It should be noted that the hexagonal form apparently results at temperatures lower than was originally thought. Thus a few hexagonal crystals occur at 60° in the growth from xylene.

(5) TWINNING.

Critical chain length for twinning.

Previous results tend to suggest a critical chain length for twinning - crystals with chains shorter than this being incapable of undergoing twinning. Thus twinning is observed in n-do-octacontane, $C_{82}H_{166}$, and n-hectane, $C_{100}H_{202}$ but not in n-nonatriacontane, $C_{39}H_{80}$. This suggests that the critical chain length lies between 39 and 82. Twins are also observed in the growth of n-propyl pentacontanoate and 19-keto-n-propyl pentacontanoate which both have a chain length of 53 carbon atoms. This suggests a critical chain length lying somewhere between 39 and 53.

In the growth of n-pentacontanol it is observed that there are a large number of twins in the growth from non-polar solvents and few in the growth from polar solvents. Further the twin layers are always bimolecular. Monomolecular twin layers have never been observed in this substance. It is therefore concluded that whereas a chain of 50 carbon atoms cannot undergo twinning a chain of 100 carbon atoms can. This conclusion is in accord with the results quoted above, and we may state that the critical chain length lies between 50 and 53.

Mechanism of twinning.

Twinning could be considered to be produced by one of two methods. It could be produced by mechanical shear as was shown for cadmium crystals by Thompson and Millard

(1952). It could also be produced by a stacking fault in the critical nucleus. However Plate VIII (Page 90) shows two co-operating spirals, one of which is twinned. This tends to suggest that twinning can occur after the formation of screw dislocations and indeed after the commencement of growth. Accordingly it is concluded that twinning is produced by mechanical shear in at least some of the crystals observed. This shear presumably occurs parallel to the basal plane of the crystal.

A further argument against production of twinning by stacking faults is that twinning occurs in bimolecular layers produced from amyl acetate. These must grow by addition of single molecules, since only such exist in this solvent. Thus any stacking fault produced in such a layer would be a fault in the stacking of single molecules and would thus produce monomolecular twin layers. A bimolecular twin layer could never be produced in this way.

The absence of twins in the crystallisation from alcohols is also inconsistent with the stacking fault mechanism. In the previous section it was shown that pseudo-double molecules participate in the crystallisation from these solvents. Thus if twinning was due to a fault in the stacking of double molecules, twins would be expected to occur as frequently in the growth from alcohols as they do in the growth from non-polar solvents. It is however possible to account for the absence of twins on the shear

theory as will be described in a later part of this section.

At first sight it might appear that since the longer chains will be more difficult to move in shear, twinning would occur in the lower members of the series and not in the higher ones. However it is presumed that the energy barrier for interconversion of the twinned and untwinned forms is greater for the longer chains. Thus although a greater shear is originally necessary, the twinned structure is more stable and does not tend to revert to the normal form.

It should be noted that although shear does not occur in the critical nucleus it must occur while the crystal is quite small otherwise the force required is impossibly large.

Since twinning is not very common among crystals grown from polar solvents it is presumed that very few bimolecular layers are formed in the growth from this group of solvents. This conclusion will be utilised in the section on nucleation and growth of n-pentacontanol.

In the bimolecular layer it is considered that on shear the double molecules must move as a single molecule otherwise we have no explanation of the exclusive occurrence of bimolecular twin layers. This is quite reasonable since independent movement of single molecules in shear would require the rupture of hydrogen bonds.

The mechanism of twinning by shear has been

discussed by Cottrell and Bilby (1951) and Thompson and Millard (1952). However these authors were chiefly concerned with explaining twinning in multimolecular crystalline layers by homogeneous shear. ~~In the present case twinning~~ is imagined to occur in mono- or bi- molecular sheets and the problem does not arise. It is of interest to note that the above authors regard a twin boundary as the line of a partial dislocation (i.e. one of fractional Burgers vector). Such a dislocation is of course equivalent to a stacking fault and thus it is to be expected that screw dislocation formation will occur on such a line. As previously stated the screw dislocations on the crystal in Plate VIII (page 90) are both centred on the twin boundary.

Temperature effect on twinning.

It was observed that no twins were observed in the growth of pentacontanol at temperatures greater than 50°. This is in accord with the results of Dawson (1952) who found no twins of n-hectane were produced at higher temperatures. It is presumed that the effect of temperature here is similar to its effect on dislocation formation. Thus a twin structure that is quite stable at room temperature may be unstable at higher temperatures by virtue of the relatively lower energy barrier.

Absence of twins in growth from alcohols.

The absence of twins in the growth from alcohol solvents is thought to be related to the fact that bimolecular layers are built up from pseudo-double molecules in this instance. This contrasts with the normal case where there is no intermediate solvent layer in the bimolecular layer. Accordingly, whereas in the latter case a monomolecular layer cannot move independently, it is considered here that the intermediate solvent layer permits such an independent movement. Such movement only involves rupture of a hydrogen bond between a solvent and solute molecule. On shear therefore, only unstable "monomolecular twins" are produced since the pseudo-double molecules do not move as single molecules.

In conclusion it should be emphasised that the present investigation still leaves us far from a clear understanding of the problem of twinning in these compounds. At best the explanations advanced in this section can only be considered to apply to the growth of the very small crystals studied in this work.

(6) NUCLEATION AND GROWTH OF N-PENTACONTANOL.

Polar solvents.

The first stage in growth from these solvents is presumably formation of a monomolecular layer, the molecules lining up in the layer with their hydroxyl groups together (Fig. 9, page 174). This regular alignment could be due to a tendency for partial hydrogen bond formation between a condensing molecule and a molecule in the lattice. Alternatively, since the hydroxyl groups are actually inclined to the chain, it could be accounted for by a terminal packing effect. It is fairly obvious that juxtaposition of the hydroxyl groups will lead to better packing. In view of the fact that a similar alignment must occur in crystals in which there are no hydrogen bonds, the second explanation is probably correct. However it is still possible that both factors are of significance.

Such a monomolecular layer can give rise to a monomolecular dislocation as discussed in section (2). Since bimolecular steps occur on some crystals, dislocations of double strength must occasionally occur and accordingly there must be at least some bimolecular layers. As was shown in section (2) these result from addition of a second layer before a dislocation is formed in the first one. It is probable that the second layer is actually formed

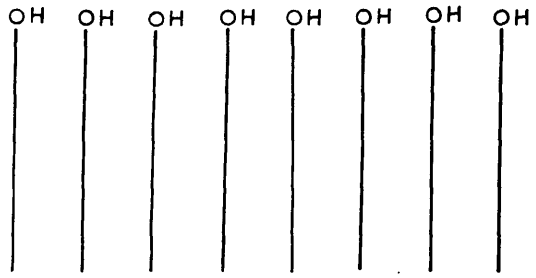

Fig. 9

Alignment of alcohol molecules in monomolecular layer.

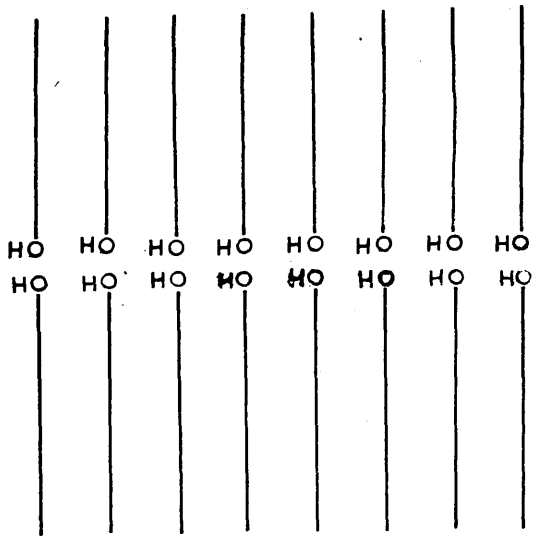

Fig. 10

Alignment of alcohol molecules in bimolecular layer.

by coalition of two already formed monomolecular layers. Evidence from the study of twist boundaries confirms this idea. To produce a regular structure the second layer must add so that the hydroxyl groups are in juxtaposition. Once again the requirements of terminal packing and the hydrogen bond will ensure that this arrangement is produced (Fig. 10, page 174). (In all the diagrams in this section the hydroxyl groups are drawn parallel to the chains for simplicity.)

These bimolecular layers can now form a bimolecular dislocation, although once again the possibility of addition of a further layer exists. That such multimolecular layers can be formed is shown by the observation of a crystal grown from amyl acetate possessing two bimolecular spirals of the same sense originating at the same point. Such a structure can only result from dissociation of a tetramolecular dislocation. Formation of a bimolecular dislocation may proceed through an intermediate stage in which a monomolecular dislocation is produced. If the solvent evaporates fairly rapidly then growth may occur on this dislocation. Some of the monomolecular spirals may be produced in this fashion. However, since very few twins are observed in the growth from polar solvents it is concluded that comparitively few bimolecular layers are produced and it is considered that very few of the monomolecular spirals arise from such a process.

Now if a bimolecular dislocation has been produced it must grow by addition of single molecules, since only these are present in solution. Normally such an addition will result in dissociation of the bimolecular step. We assume that most of the molecules adding to a step arrive by migration across the surface of the crystal and that very few molecules add to the step directly. Thus, when only single molecules condense, the bottom of a bimolecular step has a greater chance of growing and the step dissociates into two monomolecular spirals. This will only occur when no double molecules are present in solution (i.e. only in polar solvents). In agreement with this significantly more examples of step dissociation are found among crystals grown from polar solvents than on those grown from non-polar solvents (Table XI, page 121). Indeed step dissociation has never been observed on crystals grown from xylene and only on a few small crystals grown from petroleum ether. Nevertheless, on two crystals grown from amyl acetate bimolecular spirals are observed (e.g. Plate XIII, page 96). It is thought that this is accounted for by the possibilities of hydrogen bonding presented by the alcohol molecules. Consider a bimolecular step (fig. 11(a), page 177) which begins to dissociate by addition of a molecule at A. At B there is now a site for hydrogen bond formation (Fig. 11(b)). This may mean that although molecules will arrive at C by surface migration, at B there is a much greater

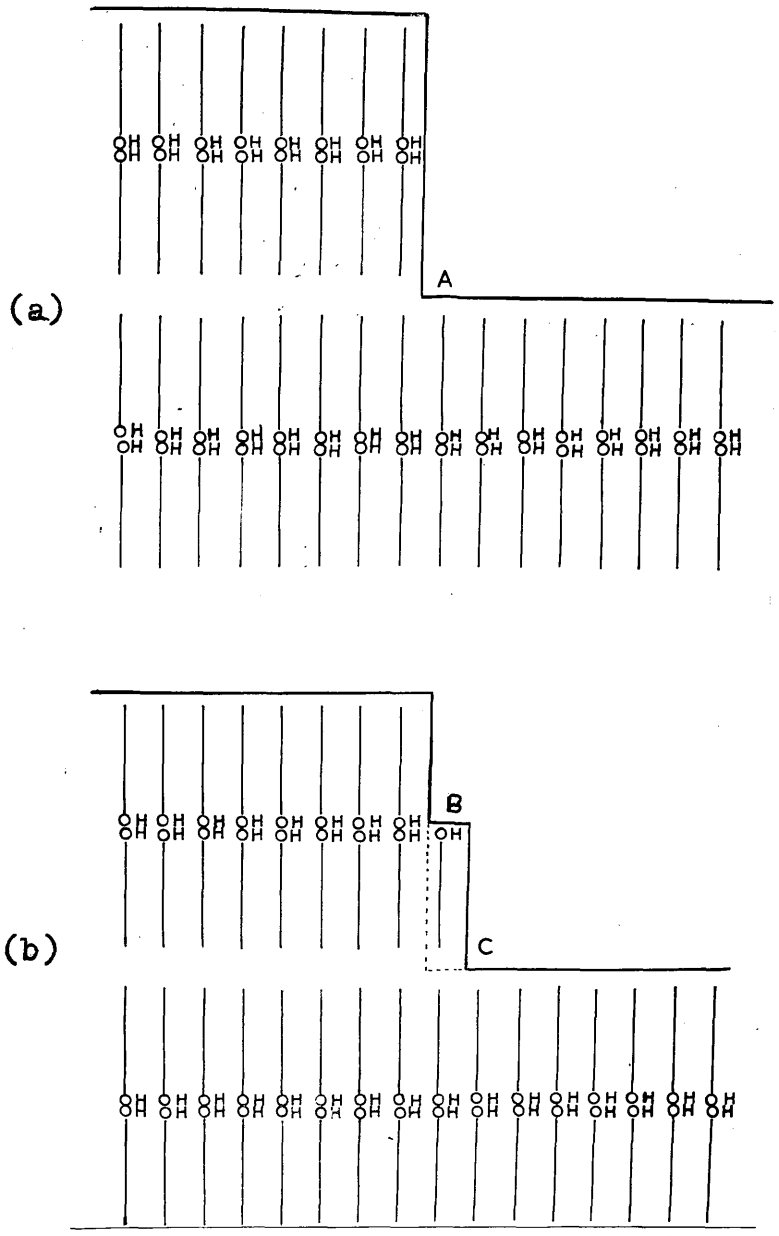

Fig. 11

Growth of bimolecular step in alcohol crystal by addition of single molecules. Addition of a molecule at A presents a hydroxyl surface at B, where addition may occur more readily than at C. Thus step dissociation is "healed".

chance of direct addition of a molecule. If the solvent evaporates slowly (as does amyl acetate), few molecules will arrive at C by migration and the dissociation may "heal" by addition of a molecule at C. Thus a bimolecular step can grow by addition of single molecules in favourable circumstances.

In most cases the above mechanism appears to fail since the bimolecular steps normally dissociate. Two possible explanations will be advanced for this.

Firstly, the number of molecules arriving at C will be determined not only by the rate of evaporation of the solvent, but also by the surface area which is available for condensation. There is, of course, a maximum limit to the size of this "collecting area" which is determined by the migration distance of the molecules. Now if we assume that the distance between the steps is less than the mean migration distance, then any molecule condensing on the surface of a step can reach a step edge. In the growth from amyl acetate the growth occurs at fairly low supersaturation and the steps are therefore fairly widely spaced. Correspondingly a fairly large number of molecules will arrive at the step edge. Thus in most cases step dissociation will occur. However if in some cases the steps are less widely spaced owing to local rapid evaporation, fewer molecules will arrive at a step by migration. Consequently the rate of direct addition by hydrogen bond formation may

be commensurate with the rate of addition by migration. Thus "healing" of the dissociation will occur immediately. The conditions in this crystallisation are thus such that there is a balance between the rates of addition by migration and by direct condensation. Consequently some bimolecular steps dissociate and others do not. Since most of the steps dissociate it is presumed that the balance is weighted in favour of addition by migration.

It is possible that at higher concentrations direct addition is favoured even where there is no possibility of hydrogen bond formation. This may be of significance in relation to the observation of multimolecular steps on cadmium iodide (Forty 1952a) and stearic acid (Reymolds and Verma 1953). These crystals were grown at fairly high supersaturation and under these conditions dissociation may not occur because of the prejudice in favour of direct addition as opposed to migration.

A second possible explanation is that the steps which dissociate arise from growth on steps such as that shown in Fig. 12(a) (page 180). Such a step if it dissociates possesses no possibilities of healing since addition of a molecule at A presents a methyl group surface at B (Fig. 12(b)). In fact direct addition would occur at C and there would be a rapid dissociation.

A step with such a structure could result from initial formation of a monomolecular layer on a formvar

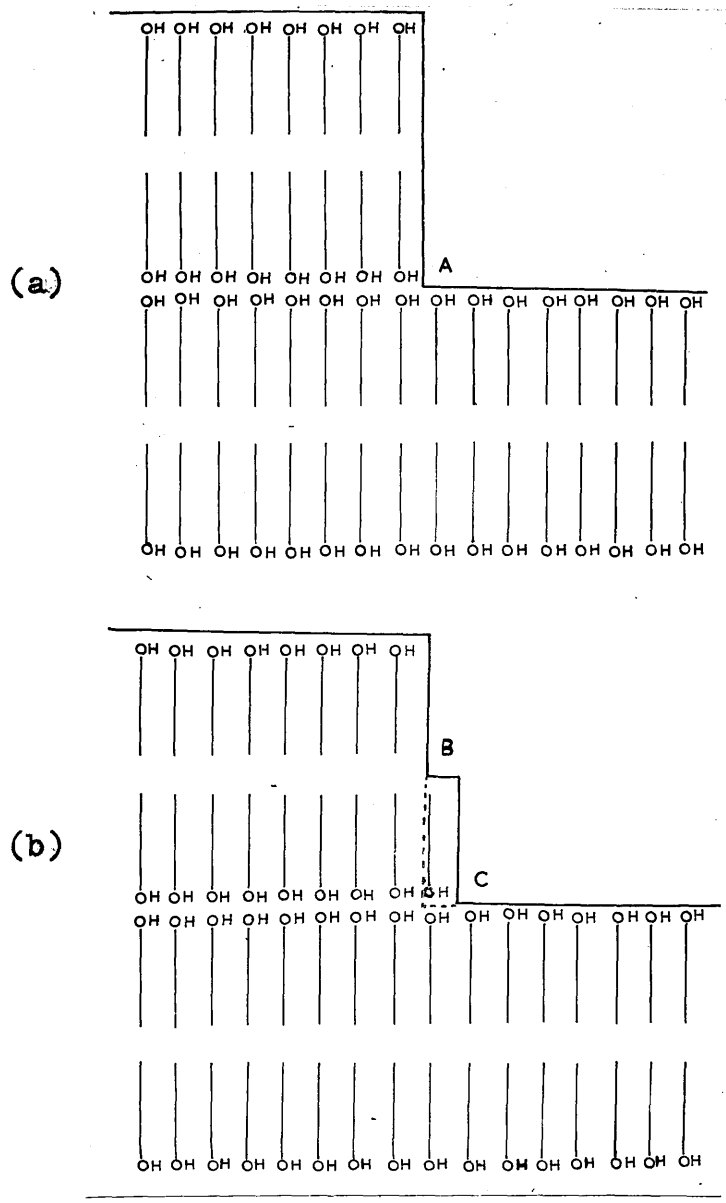

Fig. 12

Growth of bimolecular step shown in (a) by addition of single molecules at A produces methyl group surface at B as in (b). There is thus no tendency for dissociation to "heal".

film and consequent addition of a second layer which would add with the methyl groups oriented downwards. A terminal packing effect again accounts for this orientation. Now on growth such a layer will only give a spiral on the upper surface and there is no possibility of a spiral being punched through from the lower surface. It is of interest to note that whereas most of the crystals grown from amyl acetate - including those with undissociated bimolecular steps - exhibit punch through (Plates XII, XIII - page 96), those possessing dissociated bimolecular steps never do. This fact would thus tend to support the second theory.

Any decision between the two theories is rendered impossible by virtue of the fact that no other polar solvent is found which yields crystals exhibiting bimolecular and dissociated bimolecular steps. Dioxan gives no bimolecular layers and the alcohol solvents, which were originally selected as polar behave in a different manner.

Non-polar solvents.

As before the first stage in growth will be the formation of a thin layer nucleus. Now the process of nucleation involves the formation of an aggregate of molecules which is of sufficient size to have stable existence in the solid state. These are formed by non-elastic collisions between molecules resulting in adhesion. Since in in these solutions polymolecular aggregates are already

present, the process of nucleation will be more easily accomplished. Thus more primary nuclei will be formed resulting in the characteristic irregular growth observed when these solvents are used (plate V, page 86). The irregularity of the crystallisation from petroleum ether (b.p. 100 - 120°) cannot be accounted for solely on the basis of the rapid evaporation of the solvent, since the n-paraffins crystallise with extreme regularity from petroleum ether (b.p. 40 - 60°). Further the compound is capable of yielding good crystals as the results with polar solvents show. The observed irregularity can thus only be explained by the presence of the polymolecules in solution.

A monomolecular layer could be built up as described before (with addition of polymolecules as well as, or instead of, single molecules in the regular array). As before a bimolecular layer could then be formed by addition of a second layer on top of the first. However, the results discussed in section (5) on twins suggest that a large number of bimolecular layers must be formed by nucleation, since far more twins result in the growth from these solutions. Obviously double molecules can occur in the original nucleus : if there are only a few projecting from the monomolecular layer then these will only act as adsorbed molecules and will not have much stability on the surface. On the other hand, if a fairly

large number of double molecules pack into the nucleus, then the single molecules will be outnumbered. The nucleus can then be considered as a bimolecular layer with a few surface kinks at the sites of the single molecules. Such kinks will be filled rapidly.

The monomolecular layers will grow as in the growth from polar solvents. The bimolecular layers can form either a monomolecular, or a bimolecular, dislocation. If the solvent evaporates rapidly then growth may occur on the intermediately formed monomolecular dislocations. The more rapidly evaporating solvent petroleum ether might then be expected to give more monomolecular steps. Although this appears to be the case from Table III (page 115), Table VIII (page 120) showed an insignificant difference between the proportion of bimolecular steps in the growth from petroleum ether and xylene.

Crystals with bimolecular dislocations could grow by addition of single molecules as described above. However there are significantly fewer dissociated bimolecular steps in the growth from this group of solvents (Table XI, page 121). It is presumed that this is due to the double molecules in solution adding to bimolecular steps, most of which are therefore considered to grow by this mechanism.

Even if there are only small quantities of dimer present in solution, as claimed by Kreuzer and Mecke (1941), the equilibria between the various molecular types must be

preserved. Thus on removal of double molecules in growth, more are formed by a shift in the equilibria.

Thus in this group of crystallisations we have both mono- and bi-molecular steps. It might appear that this would entail a selectivity of addition for the two molecular types condensing. However if a single molecule adds to a bimolecular step, it would almost certainly be surrounded by several double molecules. Thus we would have a surface hole which would soon be filled. Similarly if a double molecule adds to a monomolecular step we have an adsorbed molecule on the surface with no real stability.

We have thus postulated a growth mechanism involving both single and double molecules. These are, of course, in equilibrium with the other polymolecular types. Since the single and double molecules are removed from solution, the equilibria will shift so that there is always a supply of these molecular types. However if the solvent evaporates rapidly there may be insufficient time for the equilibria to be re-established. Consequently polymolecular aggregates may take part in growth. Since these are monomolecular in type (i.e. they are one molecule high, although several molecules wide) they will add to monomolecular steps predominantly. Such an addition will tend to produce irregularity of the monomolecular step. The polymolecule will attempt to pack parallel to the step edge, but since addition is occurring rapidly, when it adds at a

kink it may be trapped in a position normal to the edge, by the addition of further molecules on the other side (Fig. 13, page 186). This will account for the monomolecular steps in Plate VII (page 88) being much less regular than the bi-molecular ones.

The rapid evaporation of carbon tetrachloride, resulting in extensive participation of polymolecules in growth, will account for the extreme irregularity of the crystals grown from it.

Alcohol solvents.

The growth from these solvents presents no features differing from those discussed above. The growth is more regular than from non-polar solvents. It is thought that this is due to the absence of polymolecules. It is possible to build up a pseudo-polymolecule in the same way as a pseudo-double molecule, so it must be assumed that only the dimer has any stability. It would be expected that a structure containing several solute-solvent bonds would be somewhat unstable.

Structure of pentacontanol crystals with monomolecular spirals.

It would at first sight appear that a crystal of pentacontanol with a monomolecular spiral must have a mono-molecular repeat period or possess a considerable amount of lattice disorder. However it is possible to postulate a regular structure built up from a monomolecular spiral with

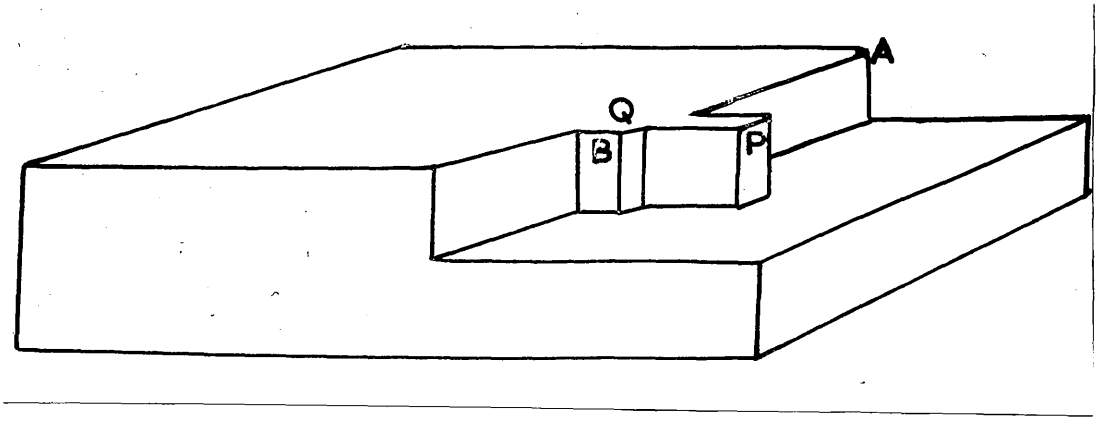

Fig. 13

Polymolecule P is prevented from aligning itself parallel to monomolecular step edge AB. Addition of single molecule at Q traps it in position normal to step edge. Thus rough step edge is produced.

a bimolecular repeat period.

Fig. 14(a) shows a monomolecular dislocation in a crystal of pentacontanol, with the hydroxyl groups oriented upwards. As single molecules add at the step their hydroxyl groups will be oriented downwards to preserve the bimolecular repeat period over the surface. This means that the molecules to the right of BD have a different vertical orientation to those molecules in the same plane situated to the left of BD (see Fig. 14(b) - page 188). As explained previously the step will turn into a spiral, but for the moment it will be supposed that it rotates as a straight line. This does not involve any differences with regard to crystalline structure, which is the main consideration in this section.

After a complete revolution we have reached the position shown in Fig. 14(b), where the complete surface has methyl groups oriented upwards. To preserve the bimolecular repeat period, molecules adding on to the step A'B' will have their methyl groups oriented downwards. Thus once again we have a reversal of orientation. This reversal will occur every time the spiral crosses the original ~~dislocation~~ slip line. Thus eventually the crystalline structure is quite regular except across this line, where the irregularity is equivalent to that which would have been produced by monomolecular slip along the line. Such an irregularity is negligible. The rest of the crystal is quite regular with a bimolecular repeat period.

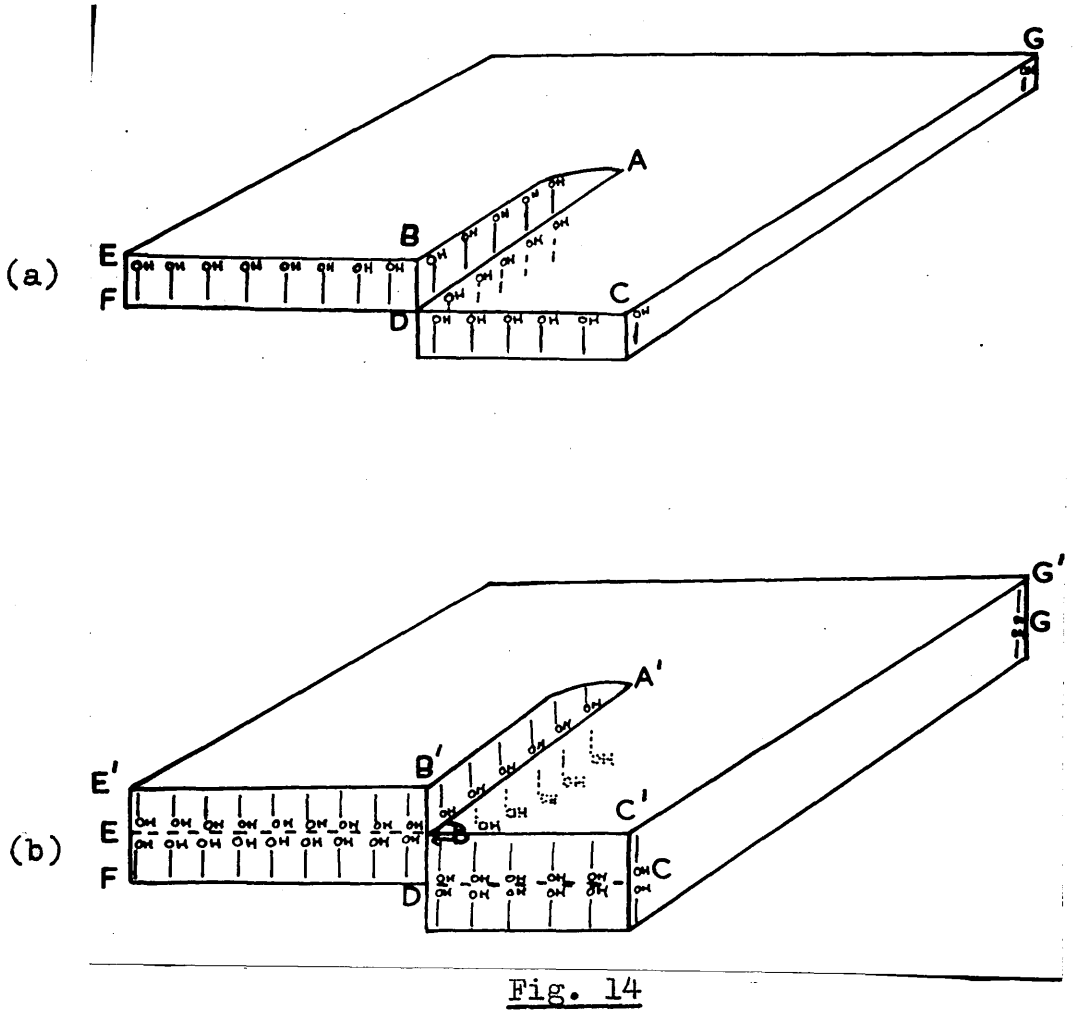

Fig. 14

(a) Monomolecular dislocation in alcohol crystal, polar surface oriented upwards.

(b) Appearance of crystal after addition of one complete molecular layer. The molecular orientation is reversed along ABD. On addition of another layer it will be similarly reversed along A'BB'.

(7) TWIST BOUNDARIES.

The problem of twist boundaries is a complicated one since there is no apparent method of controlling the conditions governing their formation. Wilman (1951) has suggested that they are produced by mechanical twist in the crystals. However this theory suffers from several serious defects.

Firstly Anderson and Dawson (1955) have shown that there is no apparent increase in the frequency of twist boundaries when crystals of n-propyl pentacontanoate are prepared by a method involving considerable pre-stressing.

Even more serious objections are revealed from structural considerations of crystals containing twist boundaries. Thus crystals such as that shown in Plate XXXVIIII (page 132) contain twist boundaries but also possess spirals on the upper and lower surface of the crystal. Thus, from elementary considerations on the structure of screw dislocations, the atoms are arranged on one continuous plane. If the twist boundary is produced by a mechanical process, then this must occur before the screw dislocation is formed. This in itself is in order if we assume initial formation of a bimolecular sheet, mechanical twist of the upper layer with respect to the lower and then formation of a monomolecular dislocation. However the case quoted occurs frequently on crystals of n-propyl pentacontanoate and the corresponding keto-ester. These compounds very rarely give bimolecular

sheets by virtue of the ready formation of a dislocation in the initially formed monomolecular sheet (see page 150). Further, even if a bimolecular sheet was formed, it would be expected to give a bimolecular dislocation at least occasionally. The spirals on the crystals described have, however, all grown from dislocations of single strength.

The twist boundary in the alcohol crystal of Plate XVII (page 99) could presumably be produced by the process considered. The three spirals are all bimolecular and of the same sense and it is known that multimolecular sheets of pentacontanol are occasionally formed. This crystal provides further evidence for the theory that twist occurs before the dislocation is formed, since here a hexamolecular dislocation has dissociated to give three bimolecular spirals one of which is at a different orientation to the other two.

On the other hand, the alcohol crystals shown in Plates X (page 93) and XX (page 103) show twist boundaries on crystals exhibiting monomolecular spirals. Since most of the alcohol bimolecular layers have the hydroxyl groups in the centre of the layer, twist over such a layer would involve rupture of the hydrogen bonds and hence is quite impossible. (Twist could occur between the sheets of a bimolecular layer of the type shown in Fig. 12, page 180. However, as stated on page 181, such a crystal would not possess a spiral on the lower surface whereas the crystal of Plate X clearly possessed spirals on both surfaces

before punch through.) Thus it is impossible to account for the structures visible on this crystal by the Wilman twist mechanism.

The only other possible mechanism is that the two sheets are formed separately and become superimposed. It is considered that they will make contact at a random angle and will attempt to attain the position of complete register. However there are certain positions of semi-stability in which the sheets are inclined and in which the molecules are not in complete register (Wilman 1951). It is thought that in certain cases the two sheets will attain this position of semi-stability and thus form a twist boundary.

This idea of superposition of sheets at an angle receives support from the fact that flat sheets are occasionally observed superimposed at an angle to each other.

The greater frequency of twist boundaries among the crystals of keto-ester grown at high supersaturation lends further support to the theory, since it is to be anticipated that under these conditions there will be a greater chance of two sheets coming into contact in the early stages of growth.

The multiple sheet can then give rise to a bimolecular dislocation which presumably will dissociate to give two monomolecular spirals of the same sense which are inclined to one another as in Plates XVII (page 99) and

and Plate XX (page 103). It should be noted that it would be impossible for the dislocation shown on the crystal of Plate XX to grow by addition of pseudo-double molecules since the two halves of the step edge are at different orientations. For this reason this case was not considered as a true example of step dissociation in the compilation of Table III (page 115).

The structure shown in Plate X (page 93) can be produced by superposition of a flat sheet on a sheet containing a screw dislocation edge. This edge would be punched through to the upper edge of the top sheet. There results a monomolecular step edge on the upper and lower surfaces. Further these two steps will give rise to two spirals at different orientations since they are eventually located in two sheets at an angle.

Twist boundaries have been observed by Wilman (1951) on crystals of the C_{16} and C_{18} alcohols, the C_{17} iodide and the paraffins containing 20 and 32 carbon atoms. They have been observed on the ester propyl pentacontanoate (Anderson and Dawson 1955) and in the present work on the corresponding keto-ester and the C_{50} alcohol. It is further considered that the sheets at differing orientations described by Amelinckx (1953b,c, 1954) for the C_{26} alcohol are better described in terms of twist boundaries.

We therefore have to explain the selective occurrence of twist boundaries on these compounds on the basis

of the theory described above. Now when the two sheets come into contact, it is presumed that they will attain the position of complete register, unless the nature of the interface is such as to prevent the sheets sliding over each other. In these circumstances the sheets will be maintained in one of the twist positions. It is fairly readily seen that the surfaces presented by the ester and keto-ester molecules will be such as to prevent slip of the sheets because of end group effects. Similarly the occurrence of twist boundaries is to be expected in iodide crystals. In this connection it should be noted that no twist boundaries were observed on the iodide crystals studied in the present work. However it should be borne in mind that twist boundaries can only be observed visually on crystals which have been punched through or which possess two spirals of the same sense. Since these structures have not been observed on the iodide crystals it is not surprising that no evidence of twist was obtained.

The occurrence of twist boundaries between two monomolecular sheets of pentacontanol can be explained in the same manner, the hydrogen bonds preventing slip. It is more difficult to account for the twist boundaries observed between bimolecular sheets. There may be a critical chain length above which the chains cannot slip over one another but in this case twist boundaries would be expected in the paraffin n-hectane whereas none were encountered.

However since so few twist boundaries were observed between bimolecular pentacontanol sheets, the reported absence of them in n-hectane may not be highly significant.

The twist boundaries in the alcohols studied by Wilman and by Amelinckx can be explained if they are between monomolecular sheets. It would however be more difficult to account for them if they are between bimolecular sheets, since any critical chain length criterion will be inoperable here. However it should be noted that these crystals possess tilted chains which may affect the process. In any case it is not clear from the descriptions of Wilman and Amelinckx exactly what type of molecular sheet is involved.

It is impossible at the present stage to account for Wilman's observation of twist boundaries in crystals of paraffin hydrocarbons. The studies of the hydrocarbon $C_{36}H_{74}$ at both high and low supersaturation have not revealed any trace of twist boundaries, although Anderson (1954) reports twist boundaries in crystals of mixed paraffins. This inconsistency serves to underline the fact that any theories on twist boundaries at the present time cannot hope to account satisfactorily for all the phenomena encountered. Until the conditions governing twist are better understood it appears dangerous to draw any conclusions from the apparent structural selectivity of twist boundary formation.

(8) SURFACE POLARITY AND GROWTH RATE.

The crystal shown in Plate VII (page 88) is remarkable in that step association occurs on three of the four crystal edges and that different pairs of steps associate on opposite edges. In the present section an attempt is made to explain these effects and to consider their importance in relation to the observations of Amelinckx (1953b,c, 1954) on cross-lacing in long chain compounds.

In section (6) it was noted that a monomolecularly grown crystal of pentacontanol would possess a "reversal line" along the original ~~dislocation~~ slip line. If we now draw a spiral with a reversal line through it (Fig. 15, page 196) it is readily seen that the molecules packed in the white and shaded areas will have different orientations. (The orientation is reversed at the reversal line and of course at monomolecular step edges.)

Let us suppose that the hydroxyl groups are oriented upwards in the shaded areas and downwards in the unshaded areas. Now it is considered that a step will advance more rapidly across a hydroxyl surface than across a hydrocarbon surface, because of the possibilities of hydrogen bond formation open to condensing molecules, which will thus have less tendency to evaporate. The steps advancing over hydroxyl surfaces will therefore tend to meet the step in front. If growth continues long enough the two steps will coalesce and will continue to grow as a bimolecular step. Thus coalition

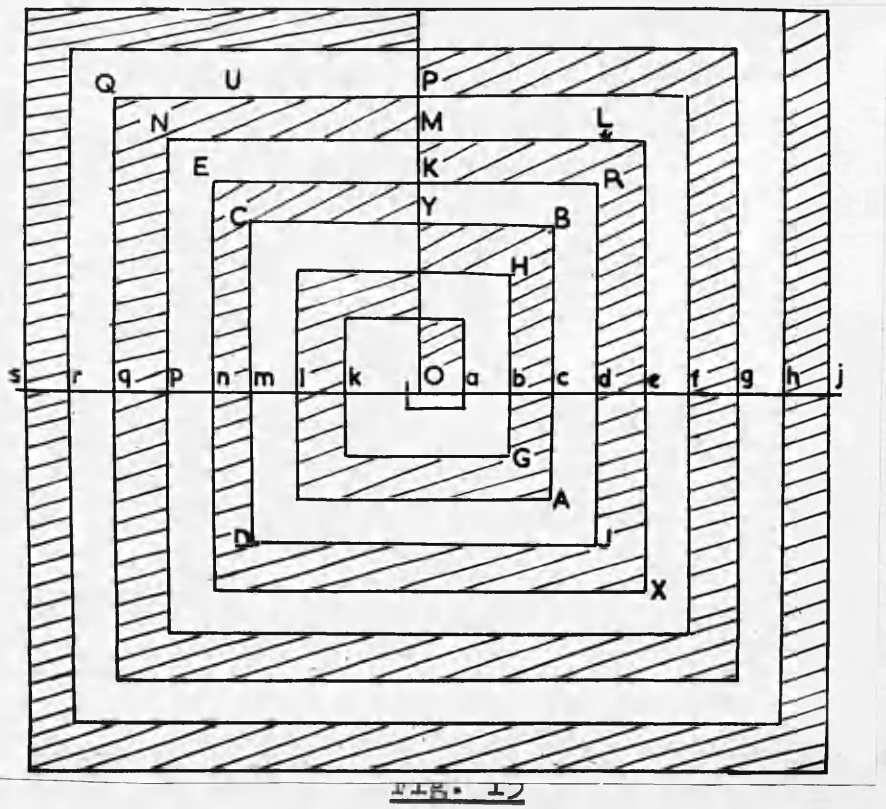

Fig. 15

Monomolecular spiral on alcohol crystal. The shaded areas areas are polar surfaces, the unshaded non-polar. OP is the reversal line.

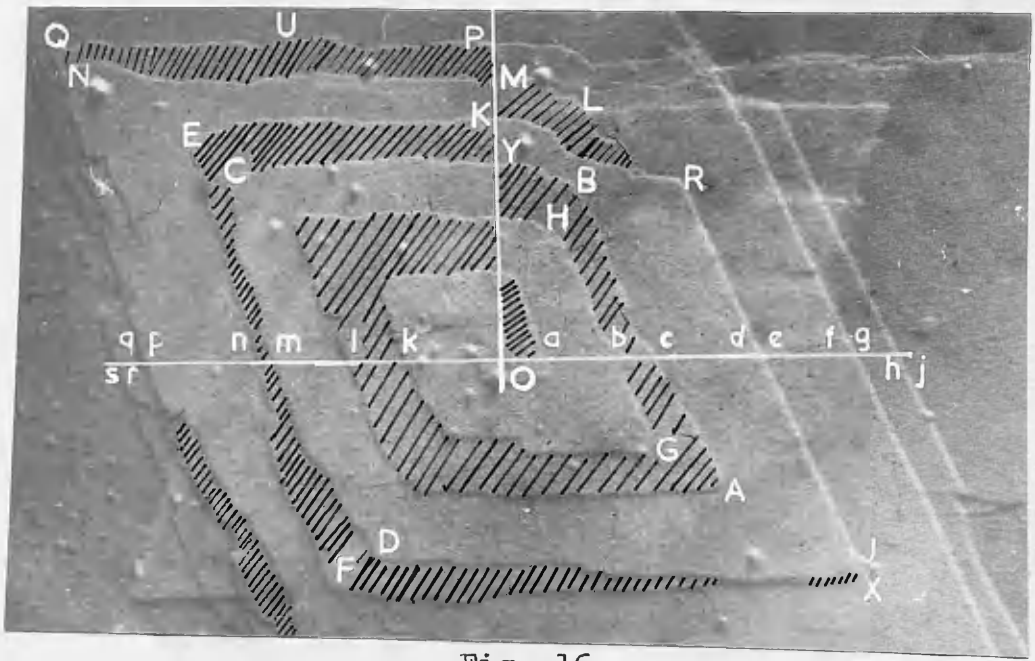

Fig. 16

Annotated photograph of crystal in Plate VII (page 88). The lettering corresponds to that in Fig. 15 (above).

of steps will occur at the outer edge of the crystal.

Let us consider the step edges AB, CD (i.e. the third step edges on the right hand sides of the crystal) in greater detail. The step CD will advance towards the next step EF, while the step AB on the other hand will be retarded by comparison and will eventually coalesce with the previous step GH. Thus we have the situation existing on the crystal in Plate VII (page 88), on which different pairs of steps coalesce on opposite crystal edges.

Thus on growth it would be expected that the distances bc, de, fg, hj would become small compared with the distances ab, cd, ef, gh. On comparison of Fig. 15 with the annotated photograph of the crystal in Plate VII (Fig. 16, page 196) it is seen that this is the case and that the distances de, fg, hj have in fact become zero since the steps have coalesced. Similarly in the opposite direction the distances kl, mn, pq, rs would be expected to become small compared with the distances lm, np, qr. Fig. 16 shows that this is indeed the case, coalition having resulted in pq and rs vanishing. (There are slight irregularities along the left hand edge, since punch through has occurred at the bottom left hand corner. This has disturbed the sequence of surface orientations and has caused anomalous step associations. The effect of punch through on the process is considered later.)

On the lower edge the step DJ will advance to

meet the step FX and so on. As can be seen from Fig. 16 on the crystal under discussion it has advanced to meet FX at one end. The two outer steps on this edge (shown on Plate VII, page 88 but not on Fig. 16) have already coalesced.

It has already been noted that no association has occurred on the upper edge of the crystal. This can be explained if we postulate that the reversal line crosses this edge. We may then suppose that initially the segment RK of the step advances towards the step in front (LM), while the segment KE is retarded, the portion YC of the previous step advancing towards it. Similarly MN advances towards PUQ (Fig. 17(a), page 199). The resultant structure is represented in Fig. 17(b) or by inversion as in Fig. 17(c). The double lines represent bimolecular steps. The portion BY represents the part of the structure nearest the crystal centre and accordingly this is the highest part of the structure. Fig. 17(d) shows a block diagram of Fig. 17(c).

Now such a structure is clearly unstable because the bimolecular steps KE, RM, PQ are linked by two monomolecular step edges KM, MP. These will clearly act as kinks and will grow to opposite corners of the crystal. This of course results in dissociation of the bimolecular steps, so that the stable structure on this edge is a series of monomolecular steps. Naturally since these steps cross the reversal line they will be linked to different steps on the two edges adjacent to the one considered.

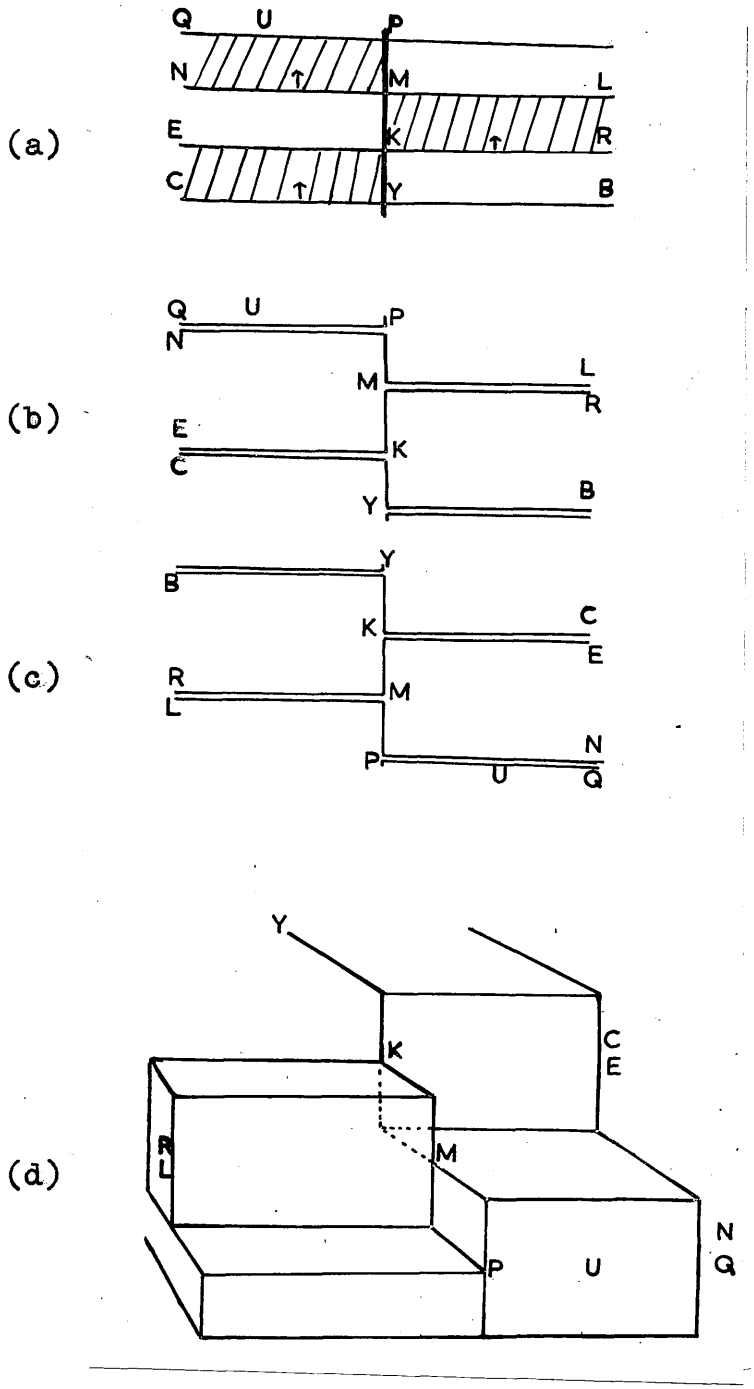

Fig. 17

Growth on "dissociation" edge of Figs. 15,16.
(a) Spiral structure on edge near reversal line.
(b) Hypothetical step structure produced by coalition of steps.
(c) Reversal of (b)
(d) Block diagram of (c). Structure is unstable because of kinks KM,MP.

Thus by assuming a structure such as that in Fig. 15 (page 196) with a reversal line as shown, we have derived a structure similar to that of the crystal shown in Plate VII, For this reason it seems that we are justified in assuming this particular orientation of the molecules and the position of the reversal line as shown in Fig. 15.

The fact that the monomolecular steps on the upper or "dissociation" edge of this crystal are linked to different steps on the adjacent edges, suggests a relation to the phenomenon of cross lacing. Further if the reversal line were to pass through the corner there would be no "dissociation edge". This means that there will be a tendency for step association on all of the edges of the crystal. The situation of the reversal line will also result in a step being linked to the step behind on one side of the corner and to the step in front on the other side. Such a structure is of course the basic cross lacing structure . Thus from a structure similar to that of the crystal in Plate VII, we can derive a cross laced structure from a vertical chain alcohol, whereas Amelinckx (1953b,c, 1954) considers that cross lacing can only occur on a tilted chain alcohol. Admittedly most of his cross laced structures are more complicated than this but it does nevertheless appear as if cross lacing can be produced other than by polytypism.

Another interesting example of the effect of surface polarity is seen on the crystal in Plate XXVI (page 108)

where differential growth after punch through has produced a cross-laced pattern. Similar phenomenon can be seen on crystal A of Plate V (page 86).

The processes of step association are incomplete in the majority of cases on the crystal of Plate XXVI (page 108). However further growth might result in these processes going to completion. This is of interest in the comparison of the results with those of Amelinckx (1953b,c, 1954) since the majority of his crystals are about 100 times the size of the average crystals studied in the present work.

In the preceding section it was seen that punch through frequently occurs at a twist boundary. Thus, if the processes described were to occur on such crystals, patterns similar to those of Amelinckx might arise. Amelinckx (1954) has denied that his crystals exhibit punch through and states that his interlaced spirals are of the same sense. However in many cases it is impossible to determine the exact structure at the dislocation centre. Further many of them possess a fairly large central terrace which is a characteristic of a crystal which has undergone further growth after punch through (Anderson and Dawson 1953).

It should however be borne in mind that the conclusions of Amelinckx apply chiefly to tilted chain alcohols and that his crystallisation conditions must be markedly different from those pertaining in the present work. Nevertheless it does appear as if cross lacing cannot be taken as conclusive evidence in favour of polytypism.

(9) EFFECT OF SUPERSATURATION ON GROWTH.

Most of the crystals grown at high supersaturations grow by normal spiral growth. This is to be anticipated since screw dislocations will be formed in any event. The result is that on nucleation a large number of nuclei are produced, which soon contain screw dislocations. Growth on this large number of dislocations will soon relieve the high supersaturation and growth will proceed normally. The essential difference between these experiments and those of Graf (1951) is that in the present instance, although the supersaturation is high, the low solubility of hexatriacontane means that the actual quantity of material in solution is small. Thus the large quantities of material required to produce the thick nuclei and lamella described by Graf are not available.

However some of the phenomena encountered can be interpreted in terms of the Graf theory. The spirals observed are generally rounded at the corners (Plate XLV, page 137) and this is consistent with the previous observations and with the ideas of Frank (1949). This means that there is an edge with a large number of kinks at the corners. Thus the highly mobile molecules condensing from the solution move over the close packed surface as described by Graf (1951) and are adsorbed at the kinked edges preferentially.

Now in the hexatriacontane lattice (Fig. 18, page 203) the axial measurements are a = 7.38A° , b = 4.94A°

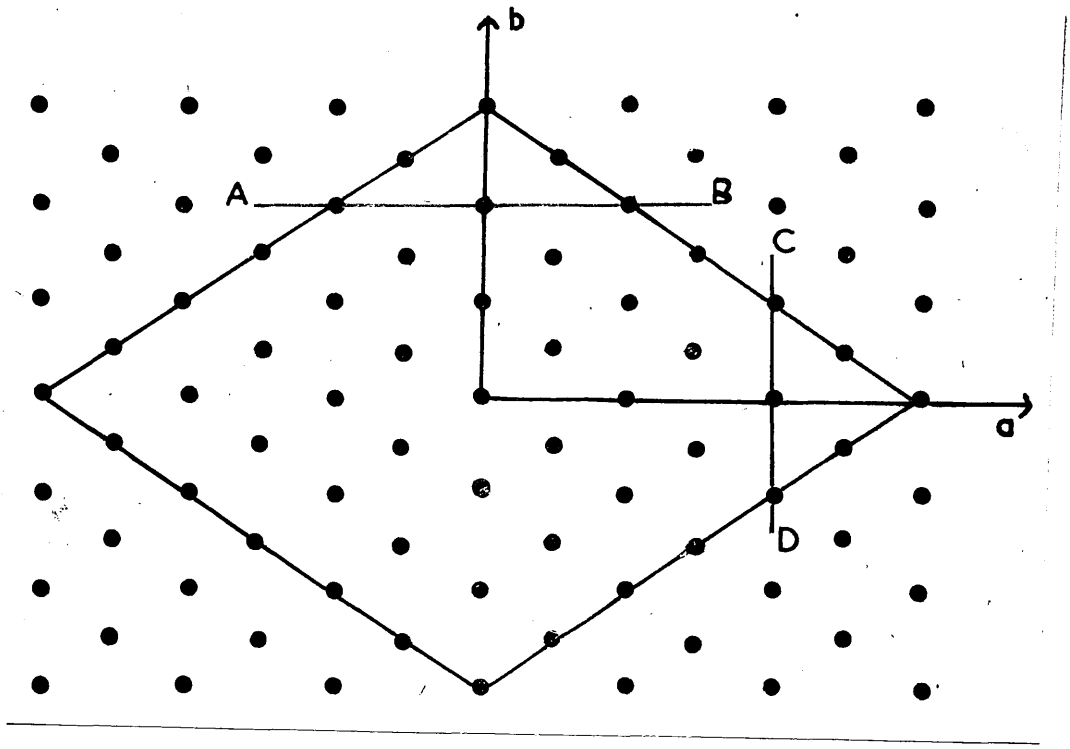

Fig. 18

Close packed and non-close packed planes in the hexatriacontane lattice. Planes such as AB are less close packed than planes such as CD. Consequently at high supersaturation growth occurs preferentially in the direction of the b-axis (i.e. in the direction of the obtuse angle of the normal crystal).

(Dawson and Vand 1951). Thus there are fewer molecules in planes such as AB parallel to the a-axis than there are in planes such as CD parallel to the b-axis. Thus planes such as AB will grow more rapidly and in the conditions of growth at high supersaturation growth will occur preferentially at corners crossed by such planes rather than at corners crossed by planes such as CD. The crystals are thus elongated in the direction of the b-axis - that is in the direction of the obtuse corner. It is clear from Plate XLV (page 137) that this crystal is elongated in the direction of the obtuse corners and this phenomenon is thus accounted for on the basis of the Graf theory.

As stated above the conditions do not normally favour production of lamellar steps. However Plate XLVII (page 139) shows a crystal with multimolecular layers. This crystal has not grown by spiral growth. This could be due to formation in a few instances of thick nuclei, which can only form a dislocation with difficulty. A better explanation is that the crystal originally grew by spiral growth and that the dislocation was cancelled by punch through. Subsequent growth would then result in a flat topped crystal which can grow by layer nucleation if the supersaturation is high enough.

The edge of the crystal in Plate XLVI (page 137) appears to have grown under conditions of greater supersaturation than the rest of the crystal. This is possibly

due to growth by evaporation of some mother liquor which was not removed in the preparation of the specimens. Growth at the edge has been by layer nucleation once again. However in this case it is thought that the growth layers are primarily monomolecular, any multimolecular layers present being the result of coalition rather than nucleation as such.

The crystallisation at 50% supersaturation does not appear to give any needle crystals of the type shown in Plate XLV (page 137). Presumably at the lower supersaturation, the condensing molecules are not so mobile and there is not such a tendency for the Graf type of growth. Further, growth does not occur so preferentially in one direction and as a result the crystals are smaller in length but greater in width than those grown at higher supersaturations. They thus bear a greater resemblance to the crystals normally obtained. It will also be noted that the corners of the crystals in this batch are sharper, in accord with previous observations. There are thus fewer kinks at the corners.

The formation of the hexagonally shaped crystals as in Plate XLVIII (page 139) can also be accounted for. The tendency towards such a form is already apparent in Plate XLV (page 137) where it is seen that the acute angle corner becomes flattened by the preferential growth at the obtuse corner. This produces a face which is fairly close packed. At the lower supersaturations there will not be such a prejudice towards growth in the direction of the

obtuse corner. Thus the crystals are not so narrow as those grown at 100% supersaturation and the tendency is towards a hexagonally shaped crystal.

It is observed that the edges of the crystals grown at 50% supersaturation are frequently fairly regular. It is thought that this may be due to the fact that when the crystals have grown at 50% supersaturation, a little growth may occur at fairly low supersaturations when most of the material has been removed from solution. This process will not tend to occur to such a great extent in the growth at 100% supersaturation. The net result will be that the crystals will retain the general form characteristic of the growth at 50% supersaturation, but there will be a regularisation of the edges in the last stages of growth.

The growth of the crystals in the direction of the acube corner will tend to produce an extension of the non-close packed face at the obtuse corner (i.e. of faces parallel to the a-axis). Now when this extension occurs it is possible that local areas of this face will be close packed and thus there will be more rapid growth on either side of such areas. On regularisation of the edges in the final stages of growth on such a complex face, a re-entrant edge will be produced as in Plate XLIX (page 141). (The tendency towards such a form is already apparent in Plate XLVIII(page 139) on the small crystal at the top.) The occurrence of these edges will be completely random - thus

some crystals will possess two re-entrant edges, some (as in Plate XLIX) will only possess one and others none. As stated previously all these cases have been observed on crystals grown at 50% supersaturation.

As anticipated there is less chance of production of multimolecular layers at 50% supersaturation. Only mono- and bi-molecular layers have been observed on crystals grown under these conditions(Plates XLVIII, XLIX).

It is likely that the effects observed on the crystals of pentacontanol, grown at about 90° with no restriction on evaporation, are due to supersaturation effects. Multimolecular layers are observed on these crystals and are probably accounted for by the extremely rapid growth. This appears all the more likely since the crystals grown at a similar temperature with a restriction on the evaporation do not exhibit multimolecular layer growth. Both sets of crystals do however contain a large proportion of the hexagonal form and this phenomenon is not therefore thought to be a supersaturation effect. Further none of the hexagonal crystals obtained by rapid evaporation possess re-entrant edges so they are thought to be a genuine polymorphic form.

The bimolecular layers observed on the keto-ester crystals of Plate XL (page 132) are probably Graf lamellar steps. They exhibit the characteristic irregular growth tip of such steps.

It is still not clear how these results are

related to the observation of multimolecular spirals by Forty (1952a) and others. However a repetition of Forty's experiment with cadmium iodide has shown two interesting features. Firstly needle like crystals have been observed and this suggests growth under conditions of high supersaturation. Secondly, spiral steps which are clearly visible earlier in the growth frequently disappear in the later stages. This may of course be due to the thickening of the crystal rendering the steps less visible but it frequently occurs without any great thickening. This observation tends to point to dissociation of multimolecular layers in the final stages of growth. A similar observation is reported by Brandstätter (1953b) for the growth of organic crystals from the vapour. There is thus a possibility that the occurrence of multimolecular spirals is a supersaturation effect and that the large steps dissociate in the final stages of growth at low supersaturation. In this connection the results of Bethge and Schaffer (1954) are of interest, since they report a few multimolecular spirals in conditions producing crystals with lamellar growth steps as the normal form.

The explanation of many of the supersaturation effects described is rather difficult. However the chief importance of these results lies in the recognition of the effects for the classification of future results.

(10) THE EFFECT OF TEMPERATURE ON GROWTH.

The effects of temperature on step height, twinning and screw dislocation formation have already been discussed.

The crystallisations of pentacontanol at 40° and 60° show that the spirals become more irregular as the temperature is raised. This is due to a two-fold effect. Burton, Cabrera and Frank (1951) showed that the number of kinks in a step is a function of $e^{-\phi/kT}$ (the symbols having the same significance as in the introduction, page 19). Thus the number of kinks increases with rising temperature. Further the migration distance of condensing molecules is a function of $e^{\phi/kT}$ and thus decreases with rising temperature. (Qualitatively this is accounted for by an increased probability of evaporation from the surface. Further the surface also contains more kinks at higher temperature and so the molecules tend to be adsorbed on the surface instead of migrating across it.) Now for a molecule to add to a step it must condense on an area of the surface whose extent is governed by the magnitude of the migration distance. The smaller this distance becomes, the fewer the number of molecules which will arrive at the step.

At higher temperatures, therefore, there are more kinks in the step and fewer molecules to fill them. Consequently the steps are rougher in outline.

The crystals grown at 50°occasionally show island

nucleation. Two possible explanations can be given for this. The critical temperature for screw dislocation formation (see page 152) in this compound appears to lie in the range 50 - 60°. If it lies fairly near 50°, since it is impossible for all the crystals to grow at an exactly uniform temperature, some may be nucleated at a temperature above the critical point. There will thus be fewer screw dislocations available for growth and thus a smaller possibility of relieving the high supersaturation necessary for the initial nucleation. This may therefore result in two dimensional nucleation at certain points.

Alternatively the greater number of surface kinks will mean that the surface is fairly rough. Such a surface may undergo two dimensional nucleation fairly readily. However Burton, Cabrera and Frank (1951) have shown that surface roughness is normally only of importance near the melting point. On the other hand there may be areas which are just rough enough to allow two dimensional nucleation to occur at lower supersaturation.

At 60° no screw dislocations are formed and all the growth is by re-nucleation and layer growth. It will be noted from Plate XXXI (page 112) that the crystals are fairly irregular and tend to be elongated. This is because the growth must of necessity occur at higher supersaturation in order that renucleation may take place. Thus the phenomena encountered in the growth at high supersaturation

are again observed. It should be noted once again that the method of specimen preparation means that any supersaturation required may be achieved.

In conclusion it should be emphasised that these temperature effects cannot be over generalised. Thus spiral growth has been observed on crystals grown from the melt and the vapour, although Bethge and Schaffer (1954) observed very few spirals on crystals of copper grown from the melt, the majority of the crystals exhibiting lamellar growth steps. The effects described here can only be taken as applicable to the long chain compounds. Thus structure is of prime importance in assessing the effects of temperature on growth. On the other hand it should be noted that the effect of temperature has not been investigated for any other type of compound.

VI - CONCLUSION

VI - CONCLUSION

(1) REVIEW OF PRESENT WORK.

The results will now be considered as a whole in terms of the general aims set out in the introduction.

It is seen that the solvent effect of association necessitates slight modifications in the Frank theory. Step height is determined by the size of the molecular unit present in solution. The presence of polymolecules in solution has been shown to cause irregular growth. The water content of the solution is also of importance in the crystallisation of compounds with polar end groups.

Temperature effects give slight modifications and in certain cases may produce conditions in which the theory is invalidated by virtue of the instability of screw dislocations.

At high supersaturation some of the effects described by Graf (1951) are observed but the general features are adequately described in terms of the Frank theory .

It is not yet absolutely certain whether polymolecular steps can be accounted for by supersaturation effects.

It has been possible to postulate a mechanism for formation of screw dislocations involving edge slip which is enhanced by the presence of stacking faults in the lattice. This mechanism is extremely structure

sensitive and results in the almost complete absence of screw dislocations in crystals of the side chain compounds. However the exact nature of the mechanism has yet to be elucidated, since the absence of extremely high resolution does not allow the study of intermediate stages in the process.

End groups produce considerable effects, especially when large end groups are packed together as in iodohentriacontane crystals. It has also been shown that growth on alternating polar and non-polar surfaces, as in the alcohols can produce cross lacing effects.

It has been possible to draw some conclusions regarding the nature of the crystalline structure in certain cases. The study of the side chain compounds and the iodides has yielded information on structure which is in general agreement with the conclusions of Stenhagen (1948) and Ställberg et. al. (1952). However, as yet, it is impossible to account for the many variations observed in the crystal structure of these compounds in terms of growth processes. Thus even if we can account for the alternation of tilted and vertical chains between the even and odd members of the alcohol series, it is impossible to explain the reversal of this trend for the higher alcohols. Similarly there is no apparent reason for the change from bimolecular to monomolecular repeat period in the iodide series.

Information has also been forthcoming on the

problem of twinning and it has been possible to postulate a twinning mechanism in the light of the results.

Twist boundaries have been observed and some conclusions drawn regarding their formation. The results tend to refute the ideas of Wilman (1951) but the exact solution of the problem is hampered by the same difficulties which beset the study of screw dislocation formation.

The work as a whole has yielded a fairly complete picture of the crystal growth of long chain compounds. An assessment has been made of the effects of structure and physical conditions on crystal growth. However it should be emphasised once again that at present these conclusions apply only to long chain compounds. Some of the conclusions drawn may be more general in their application but a more detailed analysis of other groups of compounds is required before this can be confirmed.

It can readily be seen that the elucidation of many of the effects required the molecular resolution afforded by the electron microscope. It would thus appear that, although optical techniques can yield valuable information, detailed analysis of crystal growth processes demands the use of the electron microscope.

(2) FUTURE WORK.

Despite the construction of a fairly complete picture of the growth of long chain compounds, there are still a few residual problems outstanding. It would appear desirable to carry out an electron microscope study of the growth of a tilted chain alcohol. This will render it possible to relate the results of Amelinckx (1953b,c, 1954) to the present work. A suitable compound would be dotriacontanol-1 ($C_{32}H_{65}OH$) which crystallises at room temperatures in a tilted chain form which is stable up to the melting point (Ställberg et. al. 1952).

It would also be profitable to study a secondary alcohol to assess the effect of a polar group situated in the centre of the chain rather than at the end.

It was noted earlier that Wilman (1951) reported twist boundaries on crystals of long chain paraffins with 20 and 32 carbon atoms. It would be desirable to study one of these compounds to relate the work of Wilman to that of Anderson and Dawson (1955). The 32 carbon chain compound would probably be suitable for electron microscopy.

Further work would then be based on the detailed study of compounds other than those with long chains. The aromatic compounds would appear to be a fruitful field. The preparation of polyphenyls has been described by Clar (1952) and the larger compounds of this group would possess molecules large enough to be resolved in the electron

microscope. Some of the larger condensed hydrocarbons might also be suitable. It is likely that there will be an even greater variation in the effects observed in these compounds since they do not possess a common structural basis similar to the long chain of the aliphatic compounds.

The results obtained for the long chain compounds will serve as a basis for the classification of the results for the aromatic compounds. It has already been shown how a knowledge of supersaturation effects facilitated a classification of the results for the side chain compounds. Presumably analagous situations will arise in a study of the aromatic compounds.

The study of inorganic compounds with the electron microscope presents more difficulties, since it is difficult to find suitable compounds with a large enough molecule. Thus although some of the heteropolyacids possess large molecules, they generally contain water of crystallisation without which the lattice collapses. They would thus be rather difficult to study in the electron microscope since the only method available would be replication before shadowcasting , which is not generally very satisfactory in investigations on crystals. The co-ordination compounds might be suitable but the structural chemistry and crystallography of those with larger molecules is at present not fully worked out.

Salts of organic compounds with polar end groups

(such as the soaps) might provide a convenient bridge between organic and inorganic compounds. However those which possess a large enough molecule are not really soluble in water but only form surface films. Since the main point in studying such compounds would be to ascertain the effect of crystallisation from solutions containing ions, the crystallisation from organic solvents would be valueless.

However it does appear thatto begin with a study of aromatic compounds would yield valuable results. Subsequent work will depend on the improvement in resolving power of commercial electron microscopes and in the development of techniques for crystallographic problems.

(3) IMPORTANCE OF CRYSTAL GROWTH STUDIES.

In conclusion it is of interest to consider the general importance of crystal growth studies.

At present crystal structure results have been used to interpret crystal growth results. However it is possible that in the future crystal growth studies may yield some evidence on the structure of crystals, particularly those which are unsuited to X-ray examination.

Further, association phenomena and other solvent effects have also been used to account for various growth structures. Again it is possible that the process will

be reversed in the future in certain instances.

Crystal growth studies provide one of the few methods at present available for studying dislocations and their properties which are of fundamental importance in connection with the strength of materials (Mott 1953, Read 1953).

An important development in this field has been the observation of "whiskers" on crystals of zinc (Compton, Mendizza and Arnold 1951) and tin (Koonze and Arnold 1953). These "whiskers" are found to have tensile strengths approximating to the values for an ideal crystal and it is presumed that they have grown without dislocations (Hardy 1955). The reason for this is as yet far from clear.

This observation may be of importance in view of the recent developments in the use of transistors in place of thermionic valves, which require the production of crystals containing very few dislocations. Whether the production of such a crystal can be controlled is at present uncertain. Further studies on the methods by which dislocations are produced would however yield information which would be of assistance in the solution of this problem.

Eventually after many detailed studies on crystal growth it may be possible to determine the optimum conditions for crystallisation of a certain compound. At present it is known that the habit can vary appreciably in the crystallisation of certain compounds. If the conditions

governing this apparently random process could be established, any particular habit could be produced at will. This may be important industrially where it is often desirable to modify the habit of a crystal (e.g. to prevent "caking" in storage). At present this is done by adding dyes or other additives to the solution but the process is completely empirical (Miles 1935, Buckley 1949, Whetstone 1949).

It may also be desirable to grow large crystals for optical purposes, particularly for infra-red apparatus. At present these crystals are usually grown from the melt (Menzies and Skinner 1949), although very little information is available about such crystallisations. More detailed information on this topic would plainly be of great value.

All the industrial applications described above involve empirical techniques. As Holden (1949) says : "Because of the rich diversity of phenomena attending crystal growth and because those who do grow crystals, usually do so to obtain the crystals, rather than to study the process, crystal growing remains more an art than a science." This statement epitomises the need for further fundamental research on crystal growth and indicates that such research will eventually have many valuable applications.

VII - REFERENCES

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